Keten. Part XIII.[1] Reactions of Dimethylketen with Some *N*-Alkyl Nitrones

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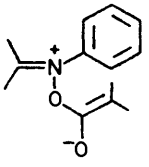
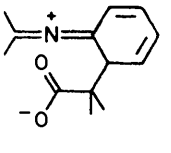
N-(Fluoroen-9-ylidene)alkylamine *N*-oxides (3) react with dimethylketen to form two series of adducts, the spiro-oxazolidinones (4) and the spiro-azetidinones (9a and b).

PREVIOUS studies[2,3] of the reactions of ketens with nitrones have employed *N*-aryl nitrones; in these reactions the initially formed zwitterion (1) undergoes a sigmatropic rearrangement [to (2)]. We report here the results of a study of the reaction of dimethylketen



(1)



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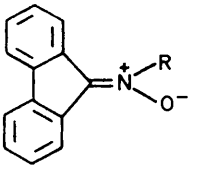


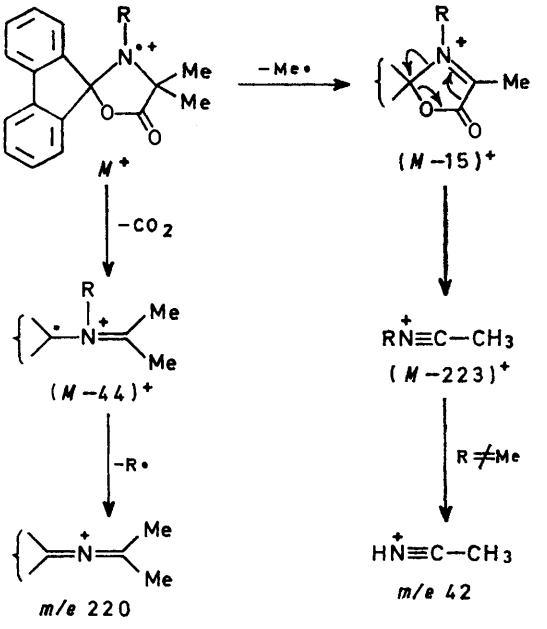
(3) a; R = Me
b; R = Et
c; R = Pr^i

with a series of *N*-alkyl nitrones in which this type of behaviour is impossible. The nitrones used (3a—c) were chosen because they afforded readily crystallisable products. Preliminary studies of similar *N*-alkyl nitrones derived from benzaldehyde and acetophenone showed that in these cases the reaction mixtures were difficult to separate.

Dimethylketen reacted with the *N*-methyl nitrone (3a) in ethyl acetate forming four products: a 1 : 1 (nitrone–keten) adduct, $C_{18}H_{17}NO_2$; a 1 : 2 adduct, $C_{22}H_{23}NO_3$, m.p. 88°; a second 1 : 2 adduct, m.p. 144°; and a compound $C_{22}H_{21}NO_2$. The last two products are still unidentified. The reaction of dimethylketen with the *N*-ethyl nitrone (3b) gave a 1 : 1 adduct, $C_{19}H_{19}NO_2$, and a 1 : 2 adduct, $C_{23}H_{25}NO_3$; the *N*-isopropyl nitrone gave only a 1 : 1 adduct, $C_{20}H_{21}NO_2$, irrespective of whether the keten was added slowly to the nitrone (the normal procedure) or *vice versa*. As well as these products, traces of fluorenone azine were sometimes isolated. No reaction was observed between the keten and the nitrones in methanolic solution.

The n.m.r. spectra of all the three 1 : 1 adducts show signals attributable to the unchanged *N*-alkyl group of the nitrone, with a six-proton singlet assigned to two methyl groups. The i.r. spectra all show a strong absorption at *ca.* 1780 cm^{-1}, and the u.v. spectra are virtually identical; these data suggest closely similar structures for the three compounds. The mass spectra show important features in common, notably the fragmentation sequence $M^+ \longrightarrow (M - 15)^+ \longrightarrow (M - 223)^+$, the last peak being the base peak in every case. All three mass spectra show a weak peak at *m/e* 220 which arises from decay of $(M - 44)^+$ in the case of the *N*-methyl and *N*-ethyl adducts. The fragments $(M - 223)^+$ in the spectra of the *N*-ethyl and *N*-isopropyl adducts decay to a common species, *m/e* 42. We believe that this evidence is best accommodated by the structure (4) for the 1 : 1 adducts, the mass spectral fragmentation being explained as shown in Scheme 1. It is not possible to explain the fragmentation pattern satisfactorily on the basis of structure (5), the expected product of a 1,3-dipolar addition between dimethylketen and the nitrone.

Support for the assigned structure (4) was sought by degradation of the *N*-isopropyl adduct. This compound was resistant to acidic hydrolysis and unaffected by



SCHEME 1

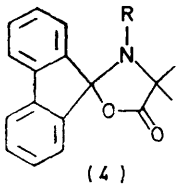
sodium borohydride or methanolic sodium methoxide. Oxidation with chromic acid gave fluorenone, proving the presence of an unchanged fluorene skeleton in the adduct. Acidic methanolysis of all the 1 : 1 adducts

[1] Part XII, G. Brooks, M. A. Shah, and G. A. Taylor, *J. Chem. Soc.* (*C*), 1973, 1297.

[2] H. Staudinger and K. Miescher, *Helv. Chim. Acta*, 1919, **2**, 554; C. H. Hassall and A. E. Lippman, *J. Chem. Soc.*, 1953, 1059.

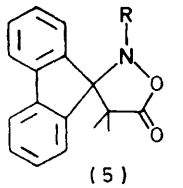
[3] R. N. Pratt, D. P. Stokes, G. A. Taylor, and P. C. Brookes, *J. Chem. Soc.* (*C*), 1968, 2086; D. P. Stokes and G. A. Taylor, *ibid.*, 1971, 2334.

gave fluorenone, and from the methanolysis of the *N*-isopropyl adduct the expected 2-isopropylaminoisobutyric acid was isolated as the methyl ester of its



(4)

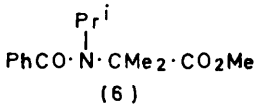
a; R = Me
b; R = Et
c; R = Pr^i



(5)

N-benzoyl derivative (6), conclusively demonstrating the structure (4c) for this adduct.

Reduction of the adduct (4c) with lithium aluminium hydride followed by work-up without exposure to acidic conditions, led to isolation of an unstable dihydro-derivative, $C_{20}H_{23}NO_2$, which was very readily hydrolysed to fluorenone by aqueous acid or base or by chromatography on silica gel. The n.m.r. spectrum of this compound in deuteriochloroform was more complicated than expected, with twice the expected number of signals due to methyl groups and two singlets at τ 0·62 and 4·82 each equivalent to about half a proton. We explain this by assignment of the hemiacetal structure (7) to the dihydro-derivative which is in equilibrium with the hydroxy-aldehyde (8) in solution. Confirmation for this proposal comes from a comparison of the i.r. spectra of a solution in chloroform with that



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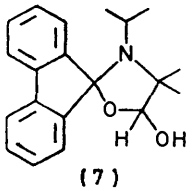

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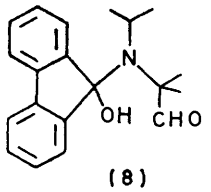
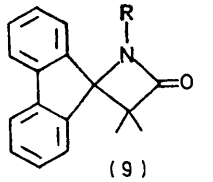


(8)

from a potassium bromide disc. The disc spectrum shows only very weak absorption in the carbonyl region with a hydroxy-group absorbing at 3544 cm^{-1}, quite distinct from the broad water absorption associated with the hygroscopic potassium bromide. The chloroform solution spectrum by contrast shows a very strong absorption at 1719 cm^{-1} with two weak absorptions at 2702 and 2803 cm^{-1} associated with C–H stretching in the aldehyde group, and a sharp hydroxy absorption at 3590 cm^{-1} with another broader peak at 3413 cm^{-1}. An n.m.r. spectrum of a dilute solution in carbon tetrachloride shows a singlet at τ 4·94 (*ca.* one proton) with no discernible absorption below τ 2, suggesting that in this solvent, as in the solid, the ring-closed isomer (7) predominates.

Comparison of the spectra of the 1 : 2 adducts of the *N*-methyl nitrone (m.p. 88°) and the *N*-ethyl nitrone reveals related features. The i.r. spectra show carbonyl absorptions at *ca.* 1730 and 1770 cm^{-1}, the u.v. spectra are closely similar, and the mass spectra contain some common fragmentation patterns. The n.m.r. spectra show clearly that in both cases the *N*-alkyl substituent of the nitrone has undergone change during the reaction, the spectrum of the *N*-ethyl nitrone adduct having signals due to a CH_3CH group, with a corresponding singlet due to a CH_2 group in the spectrum of the *N*-methyl nitrone adduct. Additionally, both spectra show signals due to two methyl groups and an isopropyl group. The spectral data, coupled with the degradative evidence given below, lead to assignment of structures (9a and b) to these compounds.



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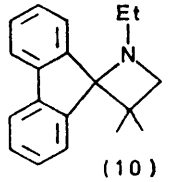


(10)

a; R = CH_2·O·COPr^i
b; R = CHMe·O·COPr^i
c; R = H
d; R = CH(OH)Me
e; R = COMe

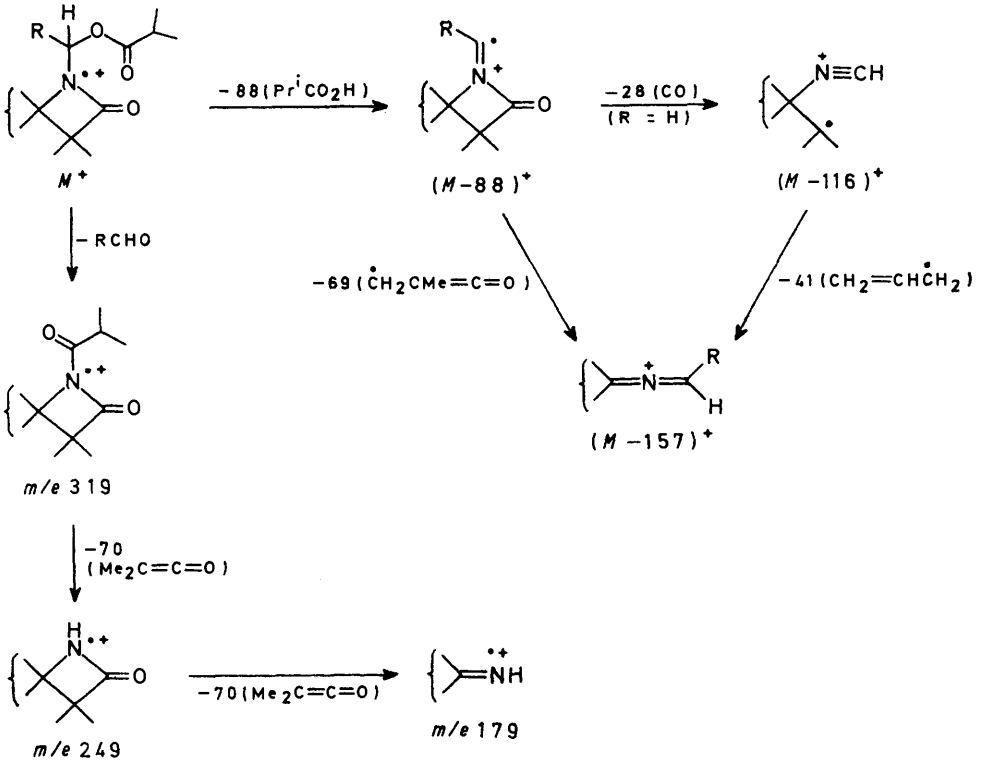
Treatment of the 1 : 2 *N*-ethyl nitrone adduct with benzylamine gave *N*-benzylisobutyramide and a compound $C_{17}H_{15}NO$. Reduction of the same adduct with an excess of lithium aluminium hydride gave a tertiary amine, $C_{19}H_{21}N$, whose n.m.r. spectrum showed signals due to eight aromatic protons and an ethyl group in which the methylene group absorbs at τ 7·44, and singlets due to a second CH_2 group (τ 6·57) and two equivalent methyl groups, consistent with the structure (10). Reduction of this adduct with a limited quantity of lithium aluminium hydride gave the previously mentioned compound, $C_{17}H_{15}NO$, as the only isolated product. This compound shows a double carbonyl i.r. absorption at 1740 and 1723 cm^{-1} and n.m.r. signals due to two equivalent methyl groups and an NH group, indicating the constitution (9c). Acidic hydrolysis of the *N*-ethyl nitrone adduct gave a compound $C_{19}H_{19}NO_2$, the n.m.r. and i.r. spectra of which lead to assignment of the constitution (9d). Reduction of this hemiacetal with lithium aluminium hydride gave mainly the tertiary amine (10) with some of the amide (9c). Oxidation of (9d) leads to a variety of products. Reaction with peracetic acid gave a low yield of fluorenone, proving the presence of an unchanged fluorene skeleton; oxidation with potassium permanganate in acetone gave the amide (9c); and oxidation with chromic acid gave the imide (9e), whose constitution was deduced from spectra.

The mass spectra of (9a and b) have several common

features, and can be rationalised in terms of the assigned structures as in Scheme 2. The mass spectrum of (9c) also has features in common with this.

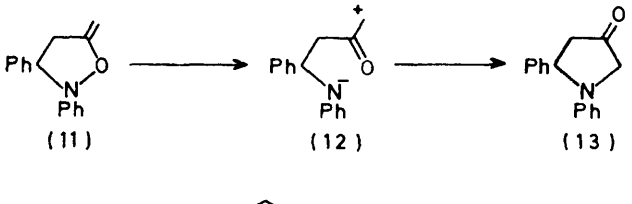
The mechanism of formation of these adducts presents a problem. Since no sign of fluorenylideneamines or their derivatives is observed, we do not think that (19) into the adducts (9a and b); this sequence is similar to that established for the reaction of *N*-benzylideneaniline *N*-oxide with dimethylketen.[3]

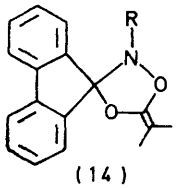
We are, so far, unable to explain why the *N*-isopropyl nitrone (3c) fails to form a 1 : 2 adduct like (9a and b). Fluorenone azine may arise from a radical process



SCHEME 2

recombination of an imine and an α-ketone arising from deoxygenation [4] can be involved, since trapping of some of the imine by dimethylketen to form a β-lactam would be expected. The failure to observe formation of the 1,3-dipolar adduct (5) is consistent with previous results in similar systems [3] and the general observation that in cycloaddition ketens do not behave like simple olefins. The reaction of allene with *N*-benzylideneaniline *N*-oxide was suggested [5] to involve initial formation of the isoxazolidine (11), which rapidly rearranged *via* a zwitterion (12) to the observed product (13). An analogous mechanism involving the dioxazolidine (14) could account for the formation of (4). However previous experience makes us favour initial formation of a zwitterion (15), which might undergo either of two [2, 3] rearrangements in which bond formation could occur at either end of the enolate ion giving the nitrenium zwitterions (16) and (17). Whilst cyclisation of (16) would give (4), the zwitterion (17), by intramolecular proton transfer, could give the imino-acid (18), which could be converted *via* the mixed anhydride leading to the species (20), which then dimerises. Traces of oxygen would form peroxides with dimethylketen and these might initiate such a process. We have observed





that alcoholic solutions of the nitrones (3) exposed to sunlight and air deposit the azine slowly, but have confirmed that the azine is formed during the reaction of dimethylketen with nitrones containing no detectable impurity.

[4] R. N. Pratt and G. A. Taylor, *J. Chem. Soc.* (*C*), 1968, 1653.
[5] M. C. Aversa, G. Cum, and N. Uccella, *Chem. Comm.*, 1971, 156.

EXPERIMENTAL

N.m.r. spectra were measured with a Varian A60 spectrometer, i.r. spectra with a Unicam SP 100 spectrometer, and u.v. spectra with a Unicam SP 700C spectrometer. Mass spectra were measured with an A.E.I. MS9 spectrometer.

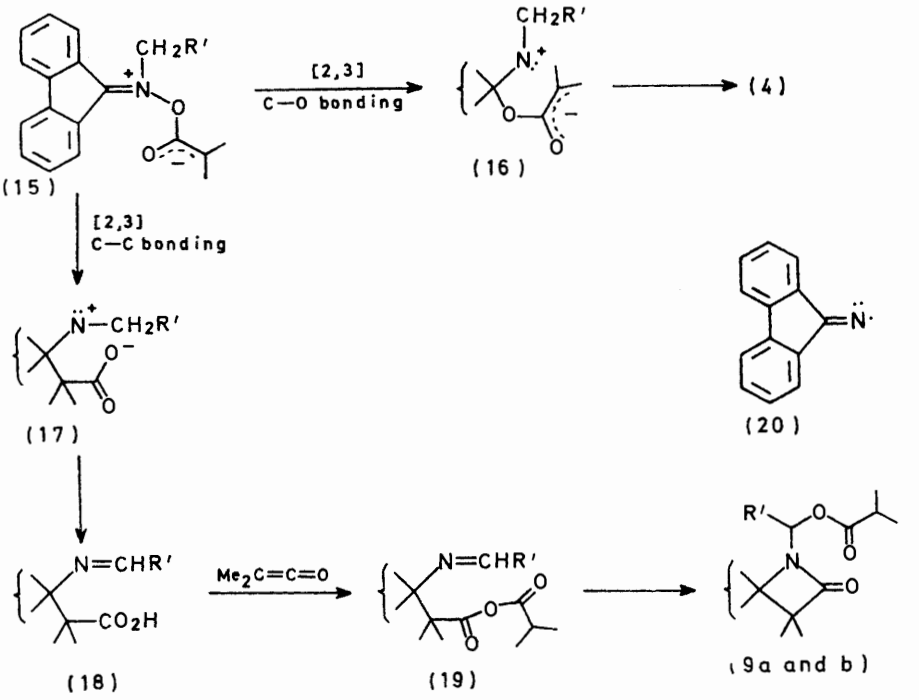
Dimethylketen was prepared by pyrolysis of tetramethylcyclobutane-1,3-dione in a modified version of Johnson and Witzel's apparatus,[6] and was used without further purification.

N-(*Fluoren-9-ylidene*)*methylamine* N-*Oxide* (3a).—Zinc dust (55 g) was added over 1½ h to a stirred mixture of nitromethane (20 g), ammonium chloride (12 g), and water (160 ml). The mixture was then filtered and the filtrate was acidified with dilute hydrochloric acid and evaporated under reduced pressure to a viscous liquid. A solution of fluorenone (15 g) in ethanol (250 ml) was added and the mixture stirred with an excess of solid sodium hydrogen carbonate until gas evolution ceased (2 h). The solution was filtered, boiled under reflux for 3 days, and evaporated to dryness. Extraction of the residue with chloroform gave the *nitrone* (3a) as yellow needles (8·2 g, 47%), m.p. 145—146° (from ethanol) (Found: C, 80·2; H, 5·3; N, 6·5. $C_{14}H_{11}NO$ requires C, 80·4; H, 5·3; N, 6·7%), $\lambda_{max.}$ (EtOH) 239, 261, 269, 301, 333, and 349 nm (log ε 4·58, 4·34, 4·29, 3·92, 4·23, and 4·35), $\nu_{max.}$ (KBr) 1279 cm^{-1}, τ ($CDCl_3$) 1·2—1·5 (1H, m), 2·4—3·0 (7H, m), and 5·88 (3H, s).

N-(*Fluoren-9-ylidene*)*ethylamine* N-*oxide* (3b), was obtained by similar procedure from nitroethane (25 g) as yellow prisms (59%), m.p. 87—88° (from ethanol) (Found: C, 80·9; H, 5·8; N, 6·2. $C_{15}H_{13}NO$ requires C, 80·7; H, 5·8; N, 6·3%), $\lambda_{max.}$ (EtOH) 239, 262, 269, 303, 335, and 351 nm (log ε 4·58, 4·34, 4·29, 3·89, 4·24, and 4·36), $\nu_{max.}$ (KBr) 1297 cm^{-1}, τ ($CDCl_3$) 1·0—1·3 (1H, m), 2·4—3·0 (7H, m), 5·66 (2H, q, *J* 7·5 Hz), and 8·46 (3H, t, *J* 7·5 Hz).

N-(*Fluoren-9-ylidene*)*isopropylamine* N-*oxide* (3c) was similarly prepared from 2-nitropropane (30 g). The crude product was dissolved in benzene and adsorbed on silica gel (350 g). After elution of unchanged fluorenone with benzene the silica was extracted with chloroform in a Soxhlet apparatus. Evaporation of the extract gave the *nitrone* (3c) as yellow plates (28%), m.p. 106—107° (from ethanol) (Found: C, 80·9; H, 6·3; N, 6·1. $C_{16}H_{15}NO$ requires C, 81·0; H, 6·3; N, 5·9%), $\lambda_{max.}$ (EtOH) 240, 262, 270, 304, 337, and 351 nm (log ε 4·60, 4·32, 4·28, 3·89, 4·24, and 4·35), $\nu_{max.}$ (KBr) 1256 cm^{-1}, τ ($CDCl_3$) 4·81 (1H, sept, *J* 6·5 Hz) and 8·43 (6H, d, *J* 6·5 Hz).

Reaction of Dimethylketen with the N-*Methyl Nitrone* (3a).—Dimethylketen (*ca.* 2 g) was passed into a solution of the nitrone (3a) (2 g) in ethyl acetate (200 ml) at room temperature and the mixture was set aside overnight. Evaporation of the solvent and shaking the residue with light petroleum gave an unidentified compound, $C_{22}H_{21}NO_2$, m.p. 177—179° (from light petroleum) (Found: C, 79·8; H, 6·3; N, 4·3. Calc. for $C_{22}H_{21}NO_2$: C, 79·8; H, 6·3; N, 4·2%). Evaporation of the mother liquor and chromatography of the residue on silica gel (elution with benzene) gave fluorenone azine (1%), followed by more of the compound $C_{22}H_{21}NO_2$ (total *ca.* 30%). Elution with ether then gave the 1 : 1 adduct 3′,4′,4′-*trimethylfluorene*-9-*spiro*-2′-*oxazolidin*-5′-*one* (4a) (8%), m.p. 154° (from light petroleum) (Found: C, 77·6; H, 6·2; N, 4·9. $C_{18}H_{17}NO_2$ requires C, 77·4; H, 6·1; N, 5·0%), $\lambda_{max.}$ (EtOH) 222, 228, 236, 268, and 275 nm (log ε 4·40, 4·51, 4·54, 4·08, and 4·07), $\nu_{max.}$ (KBr) 1782 cm^{-1}, τ ($CDCl_3$) 2·3—2·9 (8H, m), 8·00 (3H, s), and 8·41 (6H, s), *m/e* 279 (10%), 264 (23), 235(2), 220 (5), 181 (2), 180 (6), 165 (7), 70 (5), 56 (100), and 42 (3), *m** 250 (279 ⟶ 264), 206 (235 ⟶ 220), and 11·9 (264 ⟶ 56). Further elution with ether gave an



[6] J. R. Johnson and J. M. Witzel, *Org. Reactions*, 1946, **3**, 136.

unidentified 1 : 2 adduct, $C_{22}H_{23}NO_3$, as needles (7%), m.p. 144° (from light petroleum) (Found: C, 75·4; H, 6·6; N, 4·1. Calc. for $C_{22}H_{23}NO_3$: C, 75·6; H, 6·6; N, 4·0%). Continued elution with ether than gave the 1 : 2 adduct *1'-isobutyryloxymethyl-3',3'-dimethylfluorene-9-spiro-2'-azetidin-4'-one* (9a) as needles (19%), m.p. 87—88° (from light petroleum) (Found: C, 75·3; H, 6·7; N, 4·0. $C_{22}H_{23}NO_3$ requires C, 75·6; H, 6·6; N, 4·0%), $\lambda_{max.}$ (EtOH) 212, 224, 230, 238, 277, and 285 nm (log ε 3·49, 3·36, 3·44, 3·44, 3·19, and 3·02), $\nu_{max.}$ (KBr) 1778 and 1739 cm^{-1}, τ ($CDCl_3$) 2·3—2·9 (8H, m), 4·94 (2H, s), 7·75 (1H, sept, *J* 7 Hz), 8·77 (6H, s), and 9·09 (6H, d, *J* 7 Hz), *m/e* 349 (33%), 262 (9), 261 (24), 249 (11), 233 (13), 209 (27), 207 (47), 193 (21), 192 (100), 191 (57), 180 (11), 165 (27), 164 (17), 71 (23), 70 (13), 43 (47), and 41 (11), *m** 208 (261 ⟶ 233), 195 (349 ⟶ 261), 190 (192 ⟶ 191), 177 (209 ⟶ 192), 156 (209 ⟶ 180), 142 (192 ⟶ 165), 141 (261 ⟶ 192), 131, 130, and 129.

Reaction of Dimethylketen with the N*-Ethyl Nitrone* (3b).—Dimethylketen (*ca.* 2 g) was treated with the nitrone (3b) (2·2 g) in ethyl acetate (200 ml) at room temperature. Evaporation of the solution and chromatography (silica; benzene) gave fluorenone azine (0·02 g, 1%) followed by the 1 : 1 adduct *3'-ethyl-4',4'-dimethylfluorene-9-spiro-2'-oxazolidin-5'-one* (4b) as needles (0·36 g, 12%), m.p. 139—140° (from light petroleum) (Found: C, 77·7; H, 6·2; N, 4·6. $C_{19}H_{19}NO_2$ requires C, 77·8; H, 6·5; N, 4·8%), $\lambda_{max.}$ (EtOH) 222, 229, 236, 269, and 275 nm (log ε 4·39, 4·51, 4·54, 4·07, and 4·04), $\nu_{max.}$ (KBr) 1782 cm^{-1}, τ ($CDCl_3$) 2·3—2·9 (8H, m), 7·50 (2H, q, *J* 7 Hz), 8·35 (6H, s), and 9·38 (3H, t, *J* 7 Hz), *m/e* 293 (7%), 278 (23), 249 (1), 220 (5), 181 (3), 180 (6), 165 (4), 164 (6), 84 (6), 70 (100), and 42 (71), *m** 264 (293 ⟶ 278), 194·5 (249 ⟶ 220), 25·2 (70 ⟶ 42), and 17·6 (278 ⟶ 70).

Elution of the column with ether then gave the 1 : 2 adduct *1'-(1-isobutyryloxyethyl)-3',3'-dimethylfluorene-9-spiro-2'-azetidin-4'-one* (9b) as prisms (2·1 g, 60%), m.p. 94—96° (from light petroleum) (Found: C, 76·3; H, 6·6; N, 4·0. $C_{23}H_{25}NO_3$ requires C, 76·0; H, 6·9; N, 3·9%), $\lambda_{max.}$ (EtOH) 224, 230, 238, 275, 278, and 286 nm (log ε 4·66, 4·72, 4·70, 4·38, 4·37, and 4·30), $\nu_{max.}$ (KBr) 1771 and 1726 cm^{-1}, τ ($CDCl_3$) 2·1—2·8 (8H, m), 4·08 (1H, q, *J* 6·5 Hz), 7·67 (1H, sept, *J* 7 Hz), 8·69 (3H, d, *J* 6·5 Hz), 8·78 (6H, s), 8·99 (3H, d, *J* 7 Hz), and 9·02 (3H, d, *J* 7 Hz), *m/e* 363 (13%), 319 (2), 275 (30), 249 (43), 206 (87), 205 (57), 204 (43), 191 (33), 179 (26), 178 (100), 165 (26), 43 (65), and 41 (30), *m** 280·3 (363 ⟶ 319), 194·5 (319 ⟶ 249), 154·4 (275 ⟶ 206), and 177 (206 ⟶ 191).

Reaction of Dimethylketen with the N*-Isopropyl Nitrone* (3c).—Under conditions similar to those described above this gave only the 1 : 1 adduct *3'-isopropyl-4',4'-dimethylfluorene-9-spiro-2'-oxazolidin-5'-one* (4c) as needles (91%), m.p. 213° (from ethanol) (Found: C, 78·3; H, 6·8; N, 4·5. $C_{20}H_{21}NO_2$ requires C, 78·2; H, 6·8; N, 4·6%), $\lambda_{max.}$ (EtOH) 222, 229, 236, and 272 nm (log ε 4·42, 4·54, 4·57, and 4·08), $\nu_{max.}$ (KBr) 1780 cm^{-1}, τ ($CDCl_3$) 2·4—2·9 (8H, m), 6·92 (1H, sept, *J* 7 Hz), 8·27 (6H, s), and 9·23 (6H, d, *J* 7 Hz), *m/e* 307 (4%), 292 (15), 220 (3), 181 (5), 180 (3), 165 (2), 164 (6), 84 (100), and 42 (64), *m** 278 (307 ⟶ 292), 24·2 (292 ⟶ 84), and 21·0 (84 ⟶ 42).

Slow addition of a solution of the nitrone (3c) in ethyl acetate to a solution of an excess of dimethylketen in ethyl acetate led to the formation of only the adduct (4c) (82%). T.l.c. of the reaction mixture showed no sign of any other product.

Oxidation of the Adduct (4c).—Treatment with an excess of chromium trioxide in boiling aqueous acetone gave fluorenone (40%), isolated by chromatography (silica; benzene) and identified by mixed m.p.

Methanolysis of the Adduct (4c).—A solution of the adduct (4c) (2·21 g) in methanol (150 ml) and sulphuric acid (2 ml) was boiled under reflux for 24 h, then evaporated, and the residue was extracted with ether and water. Work-up of the ethereal solution gave unchanged adduct (6%) and fluorenone (1·49 g, 87%), separated by fractional crystallisation from light petroleum. The aqueous solution from the extraction was stirred overnight with benzoyl chloride (10 ml) and an excess of sodium carbonate. Extraction with ether and chromatography (silica; benzene) gave methyl benzoate and *methyl* 2-(N-*isopropylbenzamido*)-*isobutyrate* (6) (0·28 g, 15%) (Found: M^+, 263·1529. $C_{15}H_{21}NO_3$ requires *M*, 263·1521), $\nu_{max.}$ ($CHCl_3$) 1738 and 1625 cm^{-1}, τ (CCl_4) 1·8—2·8 (5H, m), 6·02 (1H, sept, *J* 7 Hz), 6·39 (3H, s), 8·43 (6H, s), and 8·78 (6H, d, *J* 7 Hz), *m/e* 263 (0·2%), 232 (3), 205 (8), 204 (58), 162 (7), 105 (100), 77 (32), 51 (5), 43 (3), 42 (6), and 41 (5).

Methanolysis of the adducts (4a and b) under similar conditions gave fluorenone (48 and 54%, respectively).

Reduction of the Adduct (4c) *with Lithium Aluminium Hydride.*—A mixture of the adduct (4c) (2 g), lithium aluminium hydride (2 g), and ether (200 ml) was boiled under reflux for 24 h. The excess of hydride was decomposed with water and the ethereal solution was filtered, washed with dilute hydrochloric acid and water, and dried (Na_2SO_4). Evaporation gave *3'-isopropyl-4',4'-dimethylfluorene-9-spiro-2'-oxazolidin-5'-ol* (7) (0·8 g, 40%), m.p. 106—107° (decomp.) (from light petroleum) (Found: C, 77·5; H, 7·5; N, 4·2. $C_{20}H_{23}NO_2$ requires C, 77·7; H, 7·4; N, 4·5%), $\lambda_{max.}$ (EtOH) 225, 232, 239, 249, 258, 274, 284, and 307 nm (log ε 4·07, 4·22, 4·37, 4·53, 4·75, 3·81, 3·78, and 3·25), $\nu_{max.}$ (KBr) 3544 and 1721w; $\nu_{max.}$ ($CHCl_3$) 3590, 3413, 2803, 2702, and 1719s cm^{-1}, τ (CCl_4) 2·2—3·0 (8H, m), 4·94 (1H, s), 7·10 (1H, sept, *J* 6·5 Hz), 7·20 (1H, s), 8·60 (3H, s), 8·63 (3H, s), 9·23 (3H, d, *J* 6·5 Hz), and 9·25 (3H, d, *J* 6·5 Hz); τ ($CDCl_3$) 0·62 (0·5H, s), 2·2—3·0 (8H, m), 4·82 (0·5H, s), 6·8—7·2br (1H, OH), 7·08 (1H, sept, *J* 6·5 Hz), 8·59 (3H, s), 8·90 (3H, s), 9·03 (3H, d, *J* 6·5 Hz), and 9·24 (3H, d, *J* 6·5 Hz). This compound is very readily hydrolysed to fluorenone under acidic conditions, and behaves like fluorenone on chromatography on silica gel.

The aqueous hydrochloric acid extract, obtained during work-up, slowly deposited fluorenone (0·08 g, 7%).

Reaction of the Adduct (9b) *with Benzylamine.*—A solution of the adduct (9b) (0·36 g) in benzylamine (5 ml) was heated at 100° overnight. After cooling, the mixture was extracted with ether and the extract washed with dilute acid and water, dried, and evaporated. Fractional crystallisation gave *N*-benzylisobutyramide (0·08 g, 49%), m.p. and mixed m.p. 92—94°, and *3',3'-dimethylfluorene-9-spiro-2'-azetidin-4'-one* (9c) (0·12 g, 49%), m.p. 226° (from benzene and light petroleum) (Found: N, 5·3. $C_{17}H_{15}NO$ requires N, 5·6%), $\lambda_{max.}$ 223, 230, 238, 279, 286, and 308 nm (log ε 4·34, 4·41, 4·36, 4·07, 3·99, and 3·13), $\nu_{max.}$ (KBr) 1740 and 1723 cm^{-1}, τ ($CDCl_3$) 2·2—2·9 (8H, m), 4·0br (1H, NH), and 8·80 (6H, s), *m/e* 249 (39%), 206 (22), 180 (70), 179 (100), 178 (24), 70 (19), 43 (26), and 41 (22), *m** 170·4 (249 ⟶ 206, loss of HNCO), 130 (249 ⟶ 180), and 128·7 (249 ⟶ 179).

Reduction of the Adduct (9b) *with Lithium Aluminium*

Hydride.—A solution of the adduct (9b) (1 g) and lithium aluminium hydride (1 g) in ether (150 ml) was boiled under reflux overnight. Work-up in the normal way gave *2′-ethyl-3′,3′-dimethylfluorene-9-spiro-2′-azetidine* (10) as needles (0·22 g, 30%), m.p. 114° (from aqueous methanol) (Found: C, 86·9; H, 8·2; N, 5·5. $C_{19}H_{21}N$ requires C, 86·7; H, 8·0; N, 5·3%), $\lambda_{max.}$ (EtOH) 226, 234, 267, 273, and 310 nm (log ε 4·38, 4·28, 4·05, 4·05, and 3·30), τ ($CDCl_3$) 2·1—2·9 (8H, m), 6·57 (2H, s), 7·44 (2H, q, *J* 7 Hz), 8·86 (6H, s), and 9·48 (3H, t, *J* 7 Hz), *m/e* 263 (32%), 262 (14), 208 (42), 207 (25), 206 (40), 192 (100), 180 (26), and 165 (29), *m** 178 (207 ⟶ 192), 164·5 (263 ⟶ 208), 163 (263 ⟶ 207), 162 (262 ⟶ 206), and 156 (208 ⟶ 180).

Reduction of (9b) under the above conditions with one fifth the quantity of lithium aluminium hydride gave (9c) (57%).

Hydrolysis of the Adduct (9b).—A suspension of the adduct (9b) (2·13 g) in aqueous hydrochloric acid (3%; 200 ml) was boiled under reflux for 1·5 h. Extraction of the mixture with chloroform gave *1′-(1-hydroxyethyl)-3′,3′-dimethylfluorene-9-spiro-2′-azetidin-4′-one* (9d), as needles (1·27 g, 74%), m.p. 187—188° (from benzene and light petroleum) (Found: C, 77·5; H, 6·5; N, 4·7. $C_{19}H_{19}NO_2$ requires C, 77·8; H, 6·5; N, 4·8%), $\lambda_{max.}$ (EtOH) 224, 231, 239, 275, 279, and 286 nm (log ε 4·35, 4·41, 4·36, 4·09, 4·09, and 4·02), $\nu_{max.}$ (KBr) 3330, 1758, and 1730 cm^{-1}, τ ($CDCl_3$) 2·1—2·8 (8H, m), 4·79 (1H, q, *J* 6·5 Hz), 6·59 (1H, s, OH), 8·77 (3H, s), 8·81 (3H, s), and 8·97 (3H, d, *J* 6·5 Hz), *m/e* (no M^+) 249 (39), 206 (41), 180 (63), 179 (100), 178 (25), 70 (18), 44 (27), 43 (26), and 41 (23).

Oxidation of Compound (9d).—(*a*) Oxidation of (9d) with hydrogen peroxide (30%) and glacial acetic acid at 100° overnight gave fluorenone (18%).

(*b*) Oxidation of (9d) with potassium permanganate in boiling acetone overnight gave the lactam (9c) (46%).

(*c*) Chromic acid (8M; 20 ml) was added to a solution of (9d) (0·3 g) in acetone (150 ml) and the mixture was boiled for 15 min. Work-up gave *1′-acetyl-3′,3′-dimethylfluorene-9-spiro-2′-azetidin-4′-one* (9e) (0·21 g, 70%) as needles, m.p. 207° (from ether and light petroleum) (Found: C, 78·0; H, 5·7; N, 4·8. $C_{19}H_{17}NO_2$ requires C, 78·3; H, 5·8; N, 4·8%), $\lambda_{max.}$ (EtOH) 228, 236, 274, 279, and 286 nm (log ε 4·46, 4·41, 4·14, 4·12, and 4·05), $\nu_{max.}$ (KBr) 1785 and 1712 cm^{-1}, τ ($CDCl_3$) 2·2—2·9 (8H, m), 7·72 (3H, s), and 8·78 (6H, s), *m/e* 291 (56%), 249 (36), 222 (49), 206 (45), 180 (68), 179 (100), 70 (58), 47 (82), and 43 (91), *m** 213 (291 ⟶ 249).

Reduction of Compound (9d) *with Lithium Aluminium Hydride*.—Reduction under conditions similar to those described above gave a mixture of the lactam (9c) (9%) and the tertiary amine (10) (37%).

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