Ketene. Part 24.[1] The Reactions of *N*-(Fluoren-9-ylidene)methylamine *N*-Oxide with Dimethylketene and Ketene

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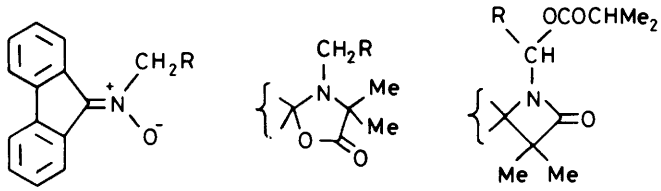
The principal products of the reaction of the *N*-methylnitrone (**1a**) with dimethylketene have been identified as the dioxolane derivative (**6**) and its hydrolysis product (**7**). Fluoren-9-yl isocyanide appears to be an intermediate in this reaction. Ketene reacts with nitrone (**1a**) and its *N*-ethyl and *N*-isopropyl analogues to give the cyclobutanedione (**15**) as the only isolated product. Compound (**15**) has been synthesized from fluoren-9-ylidenemalonic acid.

The reaction of dimethylketene with nitrones of the general structure (**1**) is known to give adducts of part-structures (**2**) and (**3**).[2] The *N*-methylnitrone (**1a**) also behaves in this way, but the compounds (**2a**) and (**3a**) account for only a small part of the total of reaction products. The major component of the isolated products was an unidentified compound, $C_{22}H_{21}NO_2$ (compound A), along with a smaller quantity of a second, also unidentified substance, $C_{21}H_{23}NO_3$ (compound B).[2] No analogous products were formed by the reaction of dimethylketene with the corresponding *N*-ethyl- and *N*-isopropylnitrones. This paper reports the investigation leading to the assignment of structures to compounds A and B.

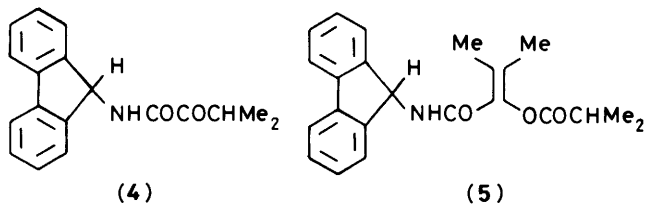
The molecular formula of compound A corresponds to the sum of one molecule of nitrone (**1a**) and two of dimethylketene less a molecule of water; that of compound B corresponds to a 1:2 (nitrone:ketene) adduct. The ratio of A to B isolated from several preparations varied considerably and it was soon found that A is hydrolysed to form B either by aqueous acid or by prolonged exposure to silica gel.

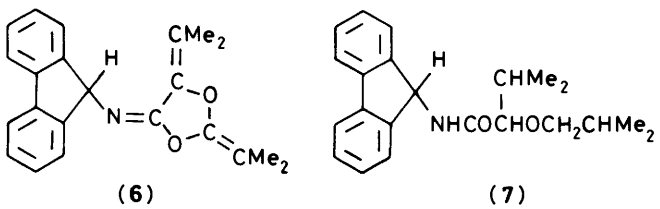
The spectra of compound A did not provide much help in assigning the structure. The i.r. spectrum showed strong absorptions at 1 764 and 1 691 cm^{-1}, but the ^{13}C n.m.r. spectrum showed no signal below δ 150, discounting the presence of a carbonyl group. The ^1H n.m.r. spectrum showed four singlets due to methyl groups and a one-proton singlet at *ca.* δ 6 with signals due to eight aromatic protons. Clearly either the *N*-methyl group of (**1a**) or one of the methyl groups of dimethylketene had been involved in the reaction. The mass spectrum was uninformative showing no significant peaks between $(M - 2)^+$ and the base peak at 165^+ (fluoren-9-yl cation). Basic hydrolysis of compound A was attempted, but after prolonged heating with methanolic sodium hydroxide only fluorenone could be identified in the products, showing that the fluorene skeleton had been preserved in compound A. Attempted reduction of compound A with lithium aluminium hydride failed, the starting material being recovered after boiling with the hydride in ether overnight.

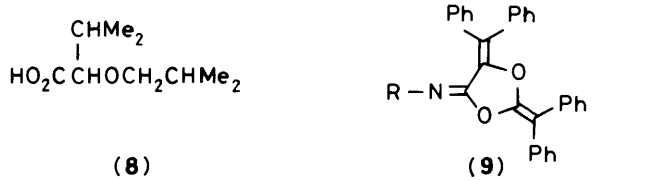
Acidic hydrolysis of compound A gave the previously reported compound B, and the i.r. spectrum of this compound showed strong absorptions at 3 300, 1 754, and 1 642 cm^{-1} and a weaker absorption at 1 675 cm^{-1}. In this case the ^{13}C n.m.r. spectrum showed two carbonyl signals at δ 163.8 and 174.7 which, together with the i.r. data, suggest the presence of amide and ester functions, both carbonyl groups being formed in the hydrolysis. The ^1H n.m.r. spectrum showed two three-proton singlets and signals due to an isopropyl group with the septet at δ 2.63, suggesting the presence of an isobutyryl group. The mass spectrum supports this interpretation, showing a significant peak at $(M - 70)^+$ (loss of dimethylketene). The lowfield resonance of the methyl singlets suggests the presence of an



a; R = H







a; R = Bu^t

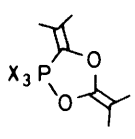
b; R = cyclohexyl

isopropylidene group, and a pair of one-proton doublets at lower field, one considerably broadened, could be due to a CHNH group.

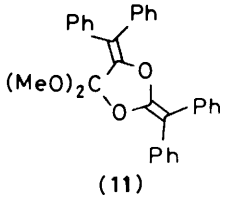
The reaction of either compound A or B with methanol and sulphuric acid gave a compound, $C_{18}H_{17}NO_2$, to which the structure (**4**) can be assigned on the basis of spectroscopic data, in particular by the presence of two carbonyl absorptions in the i.r. spectrum at 1 720 and 1 656 cm^{-1} and signals attributable to

an isopropyl group in the ^1H n.m.r. spectrum. The formation of (**4**) by methanolysis of compound B led to assignment of constitution (**5**) for compound B and thence (**6**) for compound A. Support for these proposals came from hydrogenation of compound A, which proceeded with uptake of $3H_2$ per molecule giving a product identified as (**7**) from the spectroscopic data. Proof of structure (**7**) came from an unambiguous synthesis in which 2-bromoisovaleric acid was converted into its potassium salt, which was solvolysed in isobutyl alcohol to give the acid (**8**) *via* the α-lactone. This was then converted *via* the acyl chloride into the *N*-fluorenylamide (**7**).

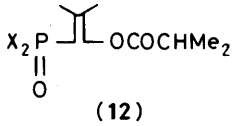
The newly formed ring structure in (**6**) is closely similar to that assigned by Ugi to the cycloadducts of diphenylketene with isonitriles[3] (**9a, b**). These adducts were degraded to compounds similar to (**4**) and (**5**). As in the case of compound A(**6**) the i.r. spectra of (**9a, b**) showed absorptions at 1 725 and 1 715 cm^{-1}, respectively, which Ugi assigned to the diphenylketene acetal group. The corresponding high frequency absorptions in the i.r. spectrum of (**6**) at 1 764 and 1 691 cm^{-1} are presumably associated with the strained double bonds around the dioxolane ring. Similar types of cycloadduct have been reported in two other cases. Trivalent phosphorus derivatives give adducts of structure (**10**; X = RO or R_2N) with dimethylketene,[4] and dimethoxycarbene adds to diphenylketene to give (**11**).[5] The i.r. spectra of these compounds have absorptions at 1 730 and 1 630 cm^{-1} and 1 680 and 1 640 cm^{-1}, respectively. Hydrolysis of (**10**) and (**11**) gives (**12**) and (**13**).



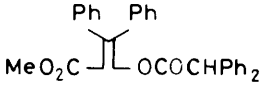
(**10**)



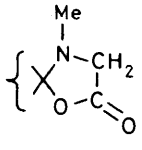
(**11**)



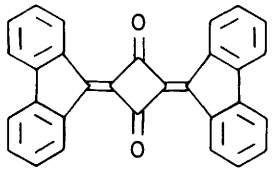
(**12**)



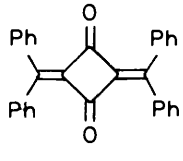
(**13**)



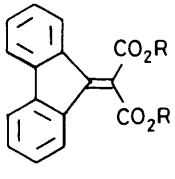
(**14**)



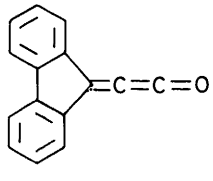
(**15**)



(**16**)



(**17**)

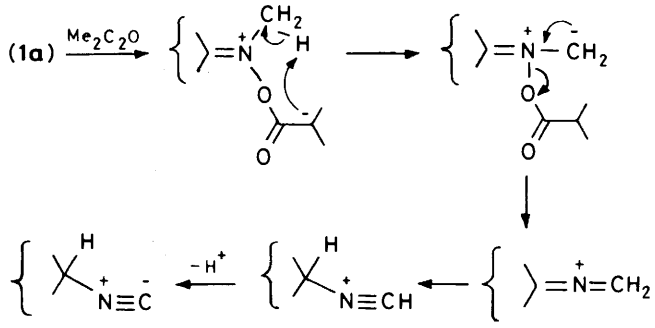


(**18**)

a; R = H

b; R = COMe

In view of Ugi's results, the formation of (**6**) from (**1a**) presumably proceeds *via* the isonitrile, which could be formed by dehydration of the *N*-methylnitrone as indicated in the Scheme. We have made several attempts to prepare the fluoren-



Scheme.

9-yl isonitrile by standard methods but have so far failed to achieve a satisfactory preparation and we have, therefore, been unable to confirm the intermediacy of this compound.

The reaction of the *N*-methylnitrone (**1a**) with ketene was also investigated. Passing a large excess of ketene into a solution of the nitrone in either ethyl acetate or benzene led to formation of a low yield of a dark, insoluble product. Use of lesser quantities of ketene did not change the product formed but gave lower yields and unchanged nitrone was identified in the reaction mixture by t.l.c. The formation of another soluble product was also shown by t.l.c. analysis of the crude reaction mixture. T.l.c. on silica gel appeared to show the formation of fluorenone, but this compound was absent from the chromatogram on alumina, which showed the presence of a new compound. All attempts to separate this new compound by chromatographic methods failed, fluorenone being the only product isolated. It is possible that an adduct of part structure (**14**) is formed in the reaction, and such a compound, lacking the steric effects of the *gem*-dimethyl groups in (**2a**), is expected to be rather easily hydrolysed.

Similar results were obtained from the reaction of ketene with the corresponding *N*-ethyl- and *N*-isopropyl-nitrones. In both cases an identical, dark, insoluble solid was formed, and t.l.c. showed the formation of soluble products which could not be isolated, fluorenone alone being obtained from chromatographic separation.

The common insoluble product from these reactions proved very difficult to characterise. It was insoluble in almost all common solvents except for chloroform in which it gave a pale purple solution with which a u.v. spectrum could be measured, but which was too dilute to enable the observation of a ^1H n.m.r. spectrum even with Fourier transform techniques. Recrystallisation by normal procedures was impossible but could be achieved by continuous extraction with a limited amount of chloroform in a Soxhlet apparatus. Acceptable microanalytical results could not be obtained and the molecular formula, $C_{30}H_{16}O_2$, was established by high resolution mass spectrometry. The i.r. spectrum showed an absorption at 1 681 cm^{-1} attributable to a carbonyl group.

Attempts to degrade this compound met with limited success. It dissolved in pyridine to give a purple solution which rapidly darkened to deep brown. No products of this reaction could be characterised. Ozonolysis of a suspension in chloroform gave fluorenone identified as its dinitrophenylhydrazone. Although quite insoluble in methanol, the compound dissolved in methanolic sodium methoxide and evaporation of this solution gave a brown solid which regenerated the original compound quantitatively on acidification. A ^1H n.m.r. spectrum of the solution in [$^2H_4$]methanol–methoxide showed only aromatic

proton signals and the mass spectrum of the material recovered from this solution on acidification showed no deuterium incorporation.

On the basis of this reversible reaction with methoxide ion, the presence in the mass spectrum of a very prominent $(M - 56)^+$ peak due to loss of two molecules of carbon monoxide, the low frequency carbonyl absorption in the i.r. spectrum, and the general pattern of the u.v.–visible spectrum in which a very strong absorption occurs at long wavelength, we guessed that the compound might be (**15**) by analogy with the known compound (**16**) which has similar spectroscopic properties and behaves in an identical way with methoxide anion.[6] Further support for the constitution (**15**) was obtained from solid state ^{13}C n.m.r. spectra using 'magic angle' rotation. These showed nine different carbon signals, five of which were attributable to non-protonated carbon atoms, entirely in accord with (**15**). The chemical shifts correlate reasonably well with those of (**16**).

To prove the structure of the insoluble compound from the reaction of ketene with (**1a**), compound (**15**) was synthesized by a known route. Diethyl fluorenylidenemalonate[7] was hydrolysed to the free acid (**17a**), which was converted into the mixed anhydride (**17b**) by reaction with ketene. This mixed anhydride when heated with potassium carbonate in benzene gave a product identical with the insoluble compound from the reaction of (**1a**). As in the analogous preparation of (**16**), this synthesis of (**15**) is assumed to proceed *via* the intermediate formation of the propadienone (**18**). It seems probable that (**18**) is also an intermediate in the pathway for formation of (**15**) from (**1a**) but we have at present no satisfactory mechanistic rationalisation for this reaction.

Experimental

^1H N.m.r. spectra were measured with Varian HA 100 and Perkin-Elmer R34 200 MHz spectrometers, and ^{13}C n.m.r. spectra with a JEOL PFT-100 spectrometer. Mass spectra were measured with Kratos MS 25 and MS 80 spectrometers. Dimethylketene was prepared by pyrolysis of tetramethylcyclobutane-1,3-dione in a modified version of Johnson and Witzel's apparatus[8] and used without further purification; ketene was prepared by pyrolysis of acetone.[9]

Reaction of Dimethylketene with the N-*Methylnitrone* (**1a**)[2].—Dimethylketene (*ca.* 7 g) was passed into a solution of the nitrone (**1a**) (5 g) in dry ethyl acetate (400 ml) and the mixture was allowed to stand at room temperature for 30 min. The mixture was evaporated under reduced pressure, the residue cooled to 0 °C, and ice-cold ethanol was added to precipitate compound A, 2,4-*dipropan*-2-*ylidene*-5-*fluoren*-9-*ylimino*-1,3-*dioxolane* (**6**) (3.6 g, 45%), m.p. 178 °C (from ethanol) (lit.,[2] 177—179 °C); $\nu_{max.}$ (KBr) 1 764 and 1 691 cm^{-1}; $\lambda_{max.}$ (EtOH) 224s, 233, 259, 269, 293, and 305 nm (log ε 4.40, 4.34, 4.42, 4.40, 4.03, and 3.99); δ_H ($CDCl_3$) 1.65 (3 H, s), 1.67 (3 H, s), 1.83 (3H, s), 1.98 (3 H, s), 5.91 (1 H, s), and 7.1—7.8 (8 H, m); δ_C ($CDCl_3$) 13.9 (Me), 14.2 (Me), 16.3 (Me), 17.9 (Me), 61.7 (CH), 115.5 (C), 118.7 (CH), 124.0 (CH), 126.3 (CH), 126.9 (CH), 133.8 (C), 139.6 (C), 144.9 (C), 147.3 (C), and 149.7 (C); *m/z* 331 (M^+, 3%), 329 (3), 207 (8), and 165 (100).

With time, the adduct (**2a**) (1 g, 15%) crystallised from the mother liquor, and t.l.c. identified fluorenone azine, fluorenone, the adduct (**3a**), and compound B (**5**) in the residues.

Acidic Hydrolysis of Compound A, (**6**).—A suspension of compound A (**6**) (0.1 g) in dilute hydrochloric acid (1M; 50 ml) was boiled under reflux for 2 h. Extraction of the mixture with ether and work-up of the ethereal solution gave compound B, N-*fluoren*-9-*yl*-3-*methyl*-2-(2-*methylpropionyloxy*)*but*-2-*enamide* (**5**) (0.07 g, 70%), m.p. 144 °C [from light petroleum (b.p. 60—80 °C)] (lit.,[2] 144 °C), $\nu_{max.}$ (paste) 3 300, 1 754, 1 675, and 1 642 cm^{-1}; $\lambda_{max.}$ (EtOH) 270, 294, and 305 nm (log ε 4.20, 3.61, and 3.62); δ_H ($CDCl_3$) 1.14 (6 H, d, *J* 7 Hz), 1.72 (3 H, s), 2.26 (3 H, s), 2.63 (1 H, sept., *J* 7 Hz), 5.99 (1 H, br d, *J* 9 Hz), 6.26 (1 H, d, *J* 9 Hz), 7.24—7.45 (4 H, m), 7.5—7.6 (2 H, m), and 7.65—7.73 (2 H, m); δ_C ($CDCl_3$) 18.8 (Me), 19.6 (Me), 33.7 (CH), 54.2 (CH), 119.9 (CH), 125.0 (CH), 127.7 (CH), 128.6 (CH), 134.3 (C), 135.1 (C), 140.4 (C), 144.1 (C), 163.8 (CO), and 174.7 (CO); *m/z* 349 (M^+, 8%), 279 (10), 180 (75), and 165 (100).

Acidic Methanolysis of Compound A (**6**).—Compound A (**6**) (0.1 g) was suspended in methanol (20 ml) and concentrated sulphuric acid (*ca.* 0.03 ml) was added. The suspended solid dissolved with the transient formation of a bright yellow colour. After 0.5 h the mixture was evaporated and the residue extracted with ether. The ethereal extract was washed with dilute aqueous sodium hydrogen carbonate, dried (K_2CO_3), and evaporated to leave N-*fluoren*-9-*yl*-3-*methyl*-2-*oxobutanamide* (**4**) (0.08 g, 95%), m.p. 178 °C [from light petroleum. (b.p. 60—80 °C)] (Found: C, 77.4; H, 6.2; N, 4.8. $C_{18}H_{17}NO_2$ requires C, 77.4; H, 6.1; N, 5.0%); $\nu_{max.}$ (KBr) 3 290, 1 720, and 1 656 cm^{-1} $\lambda_{max.}$ (EtOH) 225, 233, 268, 293, 304, 352, and 378s nm. (log ε 4.34, 4.20, 4.26, 3.63, 3.54, 1.65, and 1.40); δ_H ($CDCl_3$) 1.19 (6 H, d, *J* 7 Hz), 3.71 (1 H, sept, *J* 7 Hz), 6.10 (1 H, d, *J* 9 Hz), and 7.1—7.8 (9 H, m). Acidic methanolysis of compound B (**5**) under identical conditions also gave the amide (**4**) (88%).

Hydrogenation of Compound A (**6**).—A suspension of compound A (**6**) (0.11 g) in ethanol was shaken with palladium catalyst (10% on charcoal) under hydrogen (1 atm) for 3 h. Hydrogen absorption (23 ml) corresponded to *ca.* 3 H_2 per mole. Filtration and evaporation of the filtrate left the amide (**7**) (0.07 g, 63%) identified by i.r. and ^1H n.m.r. comparison with synthetic material.

2-*Isobutoxy*-3-*methylbutanoic Acid* (**8**).—Potassium (7.3 g) was dissolved in 2-methylpropan-1-ol (500 ml, dried by distillation from CaH_2) with heating and stirring under nitrogen. To the ice-cooled solution was added a solution of 2-bromo-3-methylbutanoic acid (34.4 g) in dry 2-methylpropan-1-ol (150 ml) and the mixture was stirred and slowly heated to boiling under reflux. Deposition of solid commenced at *ca.* 60 °C. The mixture was boiled for 0.5 h after which sodium hydrogen carbonate (21 g) was added and stirring continued at room temperature for 1 h. Most of the 2-methylpropan-1-ol was removed by fractional distillation (60—70 °C/170 mmHg) and the residue was shaken with aqueous sodium hydrogen carbonate and ether. The aqueous layer was separated, acidified, and extracted with ether. Work-up of this ethereal extract gave a pale yellow oil (18.3 g) from which fractional distillation separated the *carboxylic acid* (**8**) (7.95 g, 24%), b.p. 121—123 °C/11 mmHg; $\nu_{max.}$ (film) 3 050 and 1 720 cm^{-1}; δ_H ($CDCl_3$) 0.8—1.1 (12 H, overlapping), 1.91 (1 H, m), 2.21 (1 H, m), 3.06 (1 H, dd, *J* 7, 8.5 Hz), 3.46 (1 H, dd, *J* 6, 8.5 Hz), and 3.61 (1 H, d, *J* 5 Hz); δ_C ($CDCl_3$) 17.4, 18.9, 19.2, 19.4, 28.7, 31.7, 78.2, 84.1, and 178.3.

N-*Fluoren*-9-*yl*-2-*isobutoxy*-3-*methylbutanamide* (**7**).—A mixture of the carboxylic acid (**8**) (4 g), thionyl chloride (7 ml), and benzene (10 ml) was boiled under reflux for 2 h. Excess of thionyl chloride was removed by co-distillation with benzene and the crude acyl chloride was added to a solution of 9-aminofluorene (4 g) in dry pyridine (12 ml). After 1 h the mixture was diluted with chloroform and the chloroform solution was washed with dilute hydrochloric acid and water, and dried ($CaCl_2$). Evaporation of the solvent left the *amide* (**7**), needles (2 g, 26%), m.p. 127—128 °C (from acetic acid and water) (Found: C, 78.2; H, 8.0; N, 4.0. $C_{22}H_{27}NO_2$ requires C, 78.3; H, 8.0; N,

4.2%); $\nu_{max.}$ (paste) 3 260 and 1 645 cm^{-1}; δ_H ($CDCl_3$) 0.75 (3 H, d, *J* 8.5 Hz), 0.77 (3 H, d, *J* 8.5 Hz), 0.93 (3 H, d, *J* 7 Hz), 1.04 (3 H, d, *J* 7 Hz), 1.76 (1 H, seven line multiplet observed, nonet expected, *J* 7 Hz), 2.20 (1 H, m), 3.16 (1 H, dd, *J* 8.5, 7 Hz), 3.30 (1 H, dd, *J* 8.5, 7 Hz), 3.65 (1 H, d, *J* 4 Hz), 6.27 (1 H, d, *J* 9 Hz), 6.75 (1 H, br d, *J* 9 Hz), and 7.3—7.8 (8 H, m); δ_C ($CDCl_3$) 17.0, 19.3, 28.7, 31.9, 54.1, 78.6, 85.8, 120.0, 124.7, 125.1, 127.6, 127.7, 128.5, 128.7, 140.7, 144.1, 144.5, and 173.3.

Reaction of Ketene with the N-*Methylnitrone* (**1a**).—Ketene was passed (*ca.* 0.6 mole/h) through a solution of *N*-(fluoren-9-ylidene)methylamine *N*-oxide (1 g) in ethyl acetate (100 ml) at room temperature until t.l.c. analysis of a sample of the solution showed that all the nitrone had reacted (*ca.* 4 h). After a further hour at room temperature the mixture was filtered and the dark residue was washed with ether and purified by continuous extraction with chloroform in a Soxhlet apparatus using a small volume of solvent. 2,4-*Difluoren*-9-*ylidenecyclobutane*-1,3-*dione* (**15**) crystallised from the boiling chloroform as dark needles (0.2 g, 20%), m.p. > 300 °C [(Found mass spectrum): M^+, 408.1146. $C_{30}H_{16}O_2$ requires *m/z* 408.1150], $\nu_{max.}$ (KBr) 1 681 cm^{-1}; $\lambda_{max.}$ ($CHCl_3$) 258, 277, 284s, 322, 383s, 407, 444s, 477, 512, and 610s nm (log ε 4.49, 4.31, 4.22, 3.66, 3.71, 3.88, 3.94, 4.45, 4.73, and 3.38); *m/z* 408 (M^+, 77%), 379 ($C_{29}H_{15}O$, 13%), 352 ($C_{28}H_{16}$, 100%), 204 ($C_{15}H_8O$, 32%), and 176 ($C_{14}H_8$, 96%); δ_C (50 MHz, solid state) 121.3 (CH), 128.4 (CH), 131.1 (CH), 133.5 (CH), 137.2 (C), 143.1 (C), 147.2 (C), 152.2 (C), and 181.4 (CO).

Similar results were obtained using benzene as the solvent.

2,4-Bis(diphenylmethylene)cyclobutane-1,3-dione (**16**),[6] δ_C ($CDCl_3$) 127.9 (CH), 131.6 (CH), 132.3 (CH), 136.1 (C), 152.4 (C), 155.9 (C), and 186.5 (CO).

Ozonolysis of the Dione (**15**).—Ozone was passed through a suspension of the dione (**15**) (0.1 g) in chloroform (50 ml) until all the solid had disappeared. The orange–yellow solution was evaporated, a solution of 2,4-dinitrophenylhydrazine (5 g) in methanol (50 ml) and sulphuric acid (1 ml) was added and the mixture was boiled under reflux for 0.5 h; it was then evaporated to dryness. Extraction of the residue with chloroform and preparative t.l.c. of the chloroform-soluble material gave fluorenone 2,4-dinitrophenylhydrazone (20 mg, 11%), identified by i.r. comparison with an authentic sample.

Fluoren-9-*ylidenemalonic Acid* (**17a**).—Magnesium (0.5 g) was dissolved in a mixture of dry ethanol (30 ml) and diethyl malonate (3.4 g) with heating. When evolution of hydrogen ceased, ethanol was distilled off (20 ml) at atmospheric pressure. Xylene (30 ml) was added and distillation continued until the temperature of distillation reached 100 °C. 9,9-Dichlorofluorene (4.4 g) was added and the mixture boiled under reflux for 1 h; it was then cooled, diluted with benzene (100 ml), and washed with dilute sulphuric acid (3 × 30 ml). The organic solution was evaporated and the residue was extracted with ethanol. Aqueous sodium hydroxide (2M; 20 ml) was added and the mixture stirred overnight at room temperature. The ethanol was evaporated under reduced pressure, water (100 ml) was added, and the mixture was extracted several times with benzene until no more coloured material was extracted. Acidification of the aqueous layer precipitated a yellow–brown solid slowly. This was collected, washed with benzene, and recrystallised from ethanol and aqueous hydrochloric acid (0.05M) to give *fluoren*-9-*ylidenemalonic acid* (**17a**) as yellow needles (1 g, 20%), m.p. 201—202 °C (decomp.) (Found: C, 72.3; H, 3.7. $C_{16}H_{10}O_4$ requires C, 72.2; H, 3.8%); $\nu_{max.}$ (KBr) 1 710 and 1 695 cm^{-1}; $\lambda_{max.}$ (EtOH) 224, 263, 284, and 317 nm (log ε 4.43, 4.60, 4.03, and 4.07).

2,4-*Difluoren*-9-*ylidenecyclobutane*-1,3-*dione* (**15**).—Ketene was passed into a suspension of fluoren-9-ylidenemalonic acid (**17a**) (1.4 g) in dry benzene (30 ml) until all the solid had dissolved. The solution was purged with nitrogen to remove excess of ketene and then evaporated to dryness under reduced pressure at room temperature. The residual oil solidified to give *diacetic fluoren*-9-*ylidenemalonic dianhydride* (**17**) (1.6 g, 87%) as red crystals; $\nu_{max.}$ ($CHCl_3$) 1 822, 1 795, 1 748, 1 672, and 1 600 cm^{-1}; δ_H ($CDCl_3$) 2.30 (6 H, s) 7.0—7.7 (6 H, m), and 7.9—8.2 (2 H, m). A mixture of this anhydride (1 g), dry benzene (50 ml), and potassium carbonate (0.1 g) was boiled for 10 min. The dark brown–red mixture was filtered and the residue was washed with water, ethanol, and ether and recrystallised by continuous extraction with chloroform, as described above to give the *dione* (**15**) (0.1 g, 17%) identical in all respects with the product from the reaction of ketene with the *N*-methylnitrone (**1a**).

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