

Keten. Part 19.¹ The Reactions of 2,4,6-Trimethylbenzonitrile *N*-Oxide with Ketens

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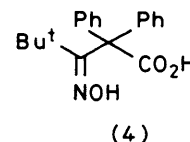
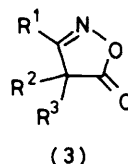
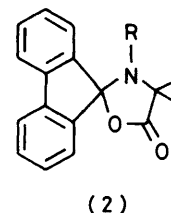
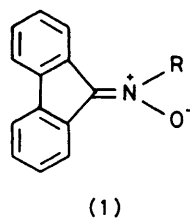
Diphenylketen, *t*-butylcyanoketen, and dimethylketen react with the title nitrile oxide to form 1 : 1 adducts shown to have the oxazolinone structures (5); keten, *t*-butylethoxycarbonylketen, and phenyl isocyanate fail to react. The nitrile oxide is deoxygenated by diphenylketen and dimethylketen; in the latter case a new type of deoxygenation process occurs forming the unsaturated ketone (11) and thence the isoxazoline (8).

The cycloadditions of ketens with nitrones are usually accompanied by rearrangements involving cleavage of the N–O bond. Thus nitrones of type (1) react with dimethylketen to give, *inter alia*, the oxazolidinones (2).² There are two reports in the literature of the cycloaddition reaction of diphenylketen with *t*-butylnitrile oxide^{3,4} and in both cases the isoxazolinone structure (3a) is assigned to the adduct. Evidence cited in support of (3a) in one of these papers³ is inconsistent with the conclusion. Alkaline hydrolysis of the adduct is reported to give a carboxylic acid (4) which is converted by acidic hydrolysis into diphenylglycine and 2,2-dimethylpropanoic acid, supposedly *via* a Beckmann rearrangement. However, heating the carboxylic acid with phosphorus pentoxide at 120 °C is also reported to reform (3a), no rearrangement occurring in this case. In our view the rearranged oxazolinone structure (5a) seemed to fit the evidence more convincingly and we have therefore examined this type of reaction again. Because of the rapid dimerisation of many nitrile oxides to furoxans, studies were conducted with the stable 2,4,6-trimethylbenzonitrile oxide.

Diphenylketen reacted with trimethylbenzonitrile oxide in boiling benzene to give two isolable products. A low yield of the expected 1 : 1 adduct was obtained and the structure of this compound was established as (5b) by alkaline hydrolysis under the conditions reported by Scarpati³ to form an amido-acid (6a) which decarboxylated above its melting point to give the simple amide (6b). This final compound was synthesised by a standard route. Spectroscopic evidence supports the structures assigned to the adduct and its hydrolysis product. The carbonyl absorption at 1 800 cm⁻¹ in the i.r. spectrum of the adduct is not diagnostic of either structures of type (3) or (5), but the corresponding absorptions in the i.r. spectrum of the product of hydrolysis at 1 718 and 1 622 cm⁻¹ clearly fit an amido-carboxylic acid. Reduction of the adduct with lithium aluminium hydride gave the amido-alcohol (6c), also identified by its spectroscopic properties. It proved impossible to reduce the sterically hindered amide group in (6c) even by prolonged and vigorous treatment with lithium aluminium hydride.

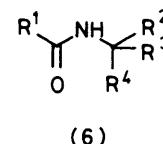
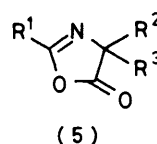
The mass spectra of these compounds provides supporting evidence for the structures assigned. In the case of the carboxylic acid (6a) and the alcohol (6c) the base peak is at *m/e* 147⁺ with an ion formula C₁₀H₁₁O, established by high resolution measurement and corresponding to the trimethylbenzoyl cation. A second weaker peak occurs at *m/e* 146⁺, C₁₀H₁₀O. The base peak in the mass spectrum of the adduct is at *m/e* 146⁺ (C₁₀H₁₀O) with a somewhat smaller peak at *m/e* 147⁺ (C₁₀H₁₁O). It seems possible that the radical cation of (5b) may transfer a hydrogen atom from one of the *o*-methyl groups of the aryl substituent onto the heterocyclic nitrogen atom before fragmentation. The ready production of these ions is not easily compatible with an isoxazolinone structure (3b).

As well as adduct formation, the reaction of diphenylketen



R¹ R² R³
 a: Bu^t Ph Ph
 b: Ar Ph Ph

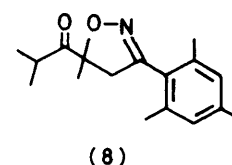
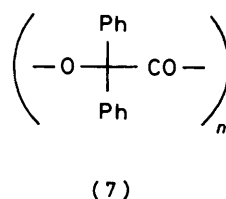
Ar = 2,4,6 - Me₃C₆H₂



R¹ R² R³
 a: Bu^t Ph Ph
 b: Ar Ph Ph
 c: Ar Bu^t CN
 d: Ar Me Me
 e: Me CF₃ CF₃

R¹ R² R³ R⁴
 a: Ar Ph Ph CO₂H
 b: Ar Ph Ph H
 c: Ar Ph Ph CH₂OH
 d: Ar Bu^t CN CO₂Me
 e: Ar Me Me CO₂H

Ar = 2,4,6 - Me₃C₆H₂



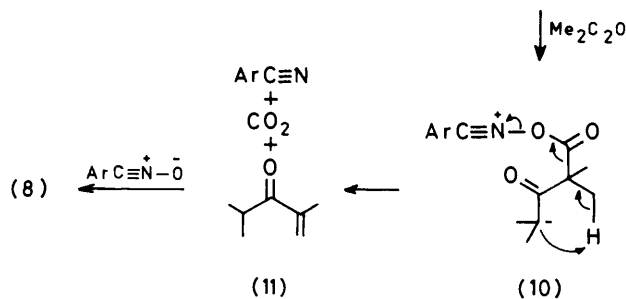
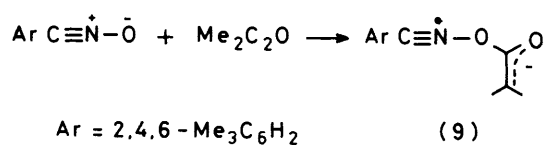
with the nitrile oxide gave a significant amount of a compound identified as the polyester of benzoic acid (7) which is known to be produced during the deoxygenation of dimethylaniline *N*-oxide by diphenylketen.⁵ The reaction residues after isolation of the adduct showed a strong absorption in the i.r. spectrum characteristic of a nitrile, but the trimethylbenzocyanitrile was not isolated as its chromatographic behaviour was very similar to that of the adduct.

t-Butylcyanoketen has been reported⁶ to behave in an anomalous way with some nitrones and its reaction with the nitrile oxide was therefore investigated. Reaction with the nitrile oxide gave the adduct (5c), which was partly methanolysed during work-up to form (6d). Here too, the spectroscopic data were entirely consistent with the structures assigned, and the mass spectra showed the strong peaks at m/e 146⁺ (C₁₀H₁₀O), and 147⁺ (C₁₀H₁₁O), although in the mass spectrum of the adduct the peak at m/e 146⁺ was due in part to a nitrogen containing species, C₁₀H₁₂N, whose ion formula corresponds to *N*-protonated trimethylbenzonitrile.

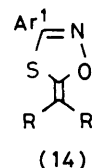
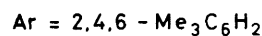
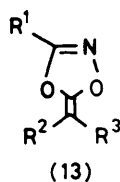
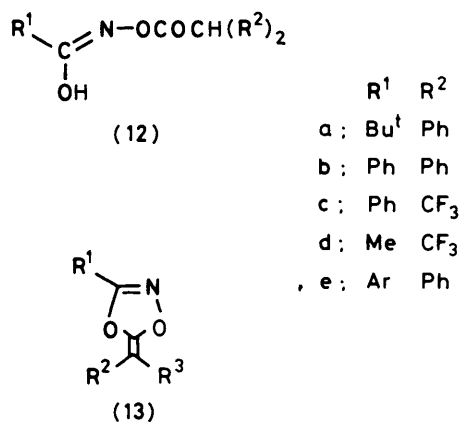
The reaction of the nitrile oxide with dimethylketen in ether at 0 °C gave two major products. One was the 1 : 1 adduct (5d) which was hydrolysed to the amido-acid (6e), structures being assigned on the basis of spectroscopic properties. Once again the mass spectra of the adduct showed the base peak at m/e 146⁺ with a smaller peak at m/e 147⁺, whilst the spectrum of the acid had the intensities reversed. The second product isolated from the reaction was a compound, C₁₇H₂₃NO₂, which was clearly not a simple adduct and was assigned the structure (8), largely from the ¹H n.m.r. spectrum which contained signals attributable to a 2,4,6-trimethylphenyl group, an isopropyl group with non-equivalent methyl groups, and a methylene group with non-equivalent protons. The ¹³C n.m.r. spectrum showed the presence of a carbonyl group, confirmed by the i.r. spectrum, and a quaternary carbon atom at δ 90.7, this chemical shift being attributed to an adjacent oxygen atom. We suggest that the Scheme rationalises the formation of compound (8). The initial formation of the zwitterion (9) is similar to the first step in the proposed mechanism for the reactions of ketens with nitrones⁶⁻⁸ and *N*-oxides,⁹⁻¹¹ and deoxygenation of the nitrile oxide by diphenylketen presumably occurs *via* a similar intermediate. Subsequent formation of the ion (10) by acylation of (9) on carbon rather than oxygen is consistent with the reactions observed between dimethylketen and phenanthridine and isoquinoline *N*-oxides,¹⁰ and the synchronous elimination and decarboxylation to form the unsaturated ketone (11) will be assisted by the good leaving group, ArCN, and the formation of carbon dioxide. The 1,3-dipolar cycloaddition of the nitrile oxide to an authentic sample of (11) gives a product identical with that isolated from the dimethylketen reaction. A possible alternative route for the formation of the intermediate (10) by the nucleophilic attack of the nitrile oxide on the cyclobutanedione dimer of dimethylketen¹² is discounted, as we have shown that these compounds do not interact over a prolonged period in boiling ether.

One consequence of the mechanism of the Scheme is the formation of the aryl cyanide. Although the nitrile was detected in the reaction mixture by g.l.c., it appeared to be present in only very low concentration. It was at first thought that it might react with nitrile oxide in a 1,3-dipolar cycloaddition to give a diaryl 1,2,4-oxadiazole,¹³ but attempts to bring about this reaction were unsuccessful, possibly for steric reasons. The alternative possibility, that of reaction between the nitrile and excess of dimethylketen, seems to have no precedent in the literature, but preliminary experiments suggest that such a reaction does occur. So far no products of this reaction have been characterised.

Attempts to bring about reaction of the nitrile oxide with keten or *t*-butyl ethoxycarbonylketen were unsuccessful. No



Scheme.



adduct formation was detected in either case, and in the latter case isomerisation of the nitrile oxide to the isocyanate occurred under the conditions employed. The ethoxycarbonylketen appears to catalyse the nitrile oxide-isocyanate interconversion, since in the absence of the keten the nitrile oxide was stable under the reaction conditions. Likewise, no sign of a reaction between the nitrile oxide and phenyl isocyanate could be detected after prolonged heating in benzene. This is somewhat surprising since isocyanates are isoelectronic with ketens and phenyl isocyanate readily deoxygenates dimethylaniline *N*-oxide.⁵

A further point of interest in Scarpati and Sorrentino's paper³ concerns the reaction of diphenylketen with nitrile oxides at -5 °C in wet ether. From these reactions the acyl derivatives of hydroxamic acids (12a,b) were isolated and their structures established by hydrolysis and independent syntheses. One pathway by which these compounds might have arisen is *via* the formation of the keten acetals (13) which

could then undergo hydrolytic cleavage to form (12). Since a [1,3] rearrangement¹⁴⁻¹⁶ of (13) involving a migration of nitrogen from oxygen to carbon would lead to oxazolinones like (5), the keten acetals (13) might be intermediates in the formation of (5), and related species could be involved in the formation of the oxazolidinone (2) from (1). It has been reported¹⁷ that bis(trifluoromethyl)keten adds to benzonitrile and acetonitrile *N*-oxides to give dioxazole adducts (13c,d), and the adduct (13d) undergoes acidic hydrolysis forming (12d).¹⁸ There is no suggestion that these adducts rearrange readily, (13c) being distilled at 110 °C/2 mmHg.¹⁷ However, the rationalisation of the mass spectrum of (13d) requires initial isomerisation of the radical cation into that of (5e).¹⁸ Elsewhere it has been reported¹⁹ that nitrile oxides add to thioketens to give adducts of structure (14).

In an attempt to discover whether (13e) was an intermediate in the formation of (5b) the nitrile oxide and diphenylketen were allowed to react in deuteriochloroform at *ca.* -25 °C, changes being followed by ¹³C n.m.r. spectroscopy. The results were inconclusive. Before the signals due to the keten had disappeared, faint signals due to (5b) had appeared, and after 32 days at -25 °C the keten had reacted and relatively strong signals at δ 161.5 and 177.4 had developed. Since the reaction is not clean it was impossible to decide whether (13e) was present, but if so it must be unstable with respect to (5b) even at the low temperature employed. An alternative explanation for the isolation of (12a,b) by Scarpati is that the diphenylketen used was converted into diphenylacetic anhydride by traces of water, and this reacted with the nitrile oxide to form the diacyl derivatives of the hydroxamic acids,²⁰ which were partly hydrolysed during work-up to give (12a,b).

Experimental

¹H n.m.r. spectra were measured with a Perkin-Elmer R34 220 MHz spectrometer, ¹³C n.m.r. spectra with a JEOL PFT-100 spectrometer, i.r. spectra with a Perkin-Elmer 457 spectrometer, and u.v. spectra with a Perkin-Elmer 559 spectrometer. Mass spectra were measured with Kratos MS25 and MS80 spectrometers. Diphenylketen was prepared by pyrolysis of benzoylphenyldiazomethane,²¹ dimethylketen by the pyrolysis of tetramethylcyclobutanedione,²² and *t*-butylcyanoketen by pyrolysis of 2,5-diazido-3,6-di-*t*-butyl-1,4-benzoxinone.²³ M.p.s were measured with a Kofler apparatus. Ether refers to diethyl ether throughout.

2,4,6-Trimethylbenzonitrile *N*-Oxide.—This compound had m.p. 112–113 °C (from methanol) (lit.,²⁴ 112–113 °C); ν_{\max} (paste) 2 285 cm⁻¹; δ_{H} (CDCl₃) 2.30 (3 H, s), 2.39 (6 H, s), and 6.90 (2 H, s); δ_{C} (CDCl₃) 20.7 (q), 21.4 (q), 110.9 (s), 128.3 (d), 140.9 (s), and 141.5 p.p.m. (s).

Reaction of 2,4,6-Trimethylbenzonitrile *N*-Oxide with Diphenylketen.—A mixture of the nitrile oxide (3.27 g), diphenylketen (from 5 g of diazoketone) and dry benzene (25 ml) was boiled under reflux for 4 h. Evaporation of the solvent left a viscous oil which, on shaking with methanol (100 ml), precipitated a yellow solid. Dissolution of this solid in ethyl acetate and reprecipitation by addition of light petroleum gave polybenzyl ester (7) (1.4 g, 33%) as an amorphous powder, m.p. 150–154 °C (lit.,⁵ 148 °C); ν_{\max} (paste) 1 750 cm⁻¹, identified by i.r. comparison with a sample prepared by oxidation of diphenylketen with dimethylaniline *N*-oxide.⁵

Evaporation of the methanol solution gave an oil which slowly crystallised on standing to give 4,4-diphenyl-2-(2,4,6-trimethylphenyl)-2-oxazolin-5-one (5b) as plates (0.65 g, 9%), m.p. 84–85 °C (from methanol) (Found: C, 80.8; H, 5.9; N, 4.2. C₂₄H₂₁NO₂ requires C, 81.1; H, 5.9; N, 3.9%); ν_{\max}

(paste) 1 800 and 1 665 cm⁻¹; λ_{\max} (EtOH) 238 nm (log ϵ 4.04); δ_{H} (CDCl₃) 2.30 (9 H, s), 6.91 (2 H, s), 7.3–7.45 (6 H, m), and 7.55–7.7 (4 H, m); δ_{C} (CDCl₃) 20.1, 21.2, 123.7, 126.6, 128.3, 128.7, 137.5, 139.2, 140.9, 161.5, and 177.4 p.p.m.; *m/e* 355 (*M*⁺, 13%), 311 (C₂₃H₂₂N, 83), 166 (C₁₃H₁₀, 57), 165 (81), 147 (C₁₀H₁₁O, 72), 146 (C₁₀H₁₀O, 100), 145 (C₁₀H₁₁N, 22), 130 (C₉H₈N, 34), and 119 (C₉H₁₁, 18).

After removal of the crystalline material, the residual oil showed a strong absorption in the i.r. spectrum at 2 220 cm⁻¹.

Hydrolysis of the Adduct (5b).—A mixture of the finely powdered adduct (5b) (1 g) and aqueous sodium hydroxide solution (15 ml; 10M) was stirred at room temperature for 4 days. The suspension was diluted with water to dissolve all the solid and acidified with sulphuric acid which precipitated 2,2-diphenyl-2-(2,4,6-trimethylbenzoylamino)ethanoic acid (6a) (0.7 g, 67%), m.p. 219–221 °C (decomp.) (from acetic acid) (Found: C, 76.9; H, 6.5; N, 3.9. C₂₄H₂₃NO₃ requires C, 77.2; H, 6.2; N, 3.8%); ν_{\max} (paste) 3 360, 2 580, 1 718, and 1 622 cm⁻¹; δ_{H} (C₅D₅N) 2.14 (3 H, s), 2.35 (6 H, s), 6.79 (2 H, s), 7.2–7.45 (6 H, m), 8.12 (4 H, d, *J* 8 Hz), 8.8 (1 H, br), and 9.47 (1 H, s); the signals at δ 8.8 and 9.47 disappeared on treatment with D₂O; δ_{C} (C₅D₅N) 19.4, 20.9, 70.6, 127.6, 127.9, 128.6, 130.0, 135.1, 136.1, 138.0, 142.3, 169.4, and 174.2 p.p.m.; *m/e* 373 (*M*⁺, 0.2%), 329 (C₂₃H₂₃NO, 31), 167 (C₁₃H₁₁, 46), 147 (C₁₀H₁₁O, 100), 146 (C₁₀H₁₀O, 8), and 119 (C₉H₁₁, 21).

***N*-(2,4,6-Trimethylbenzoyl)diphenylmethylamine (6b).**—(a) A sample of the carboxylic acid (6a) was heated above its m.p. and maintained at that temperature until carbon dioxide evolution ceased. On cooling, the melt solidified forming the amide (6b) (quantitative yield), m.p. 153–154 °C (from acetic acid) (Found: C, 83.6; H, 7.0; N, 3.9. C₂₃H₂₃NO requires C, 83.9; H, 7.0; N, 4.3%); ν_{\max} (paste) 3 260 and 1 632 cm⁻¹; δ_{H} (CDCl₃) 2.22 (s) and 2.24 (s) (total 9 H), 6.33 (1 H, br d, *J* 8 Hz), 6.50 (1 H, d, *J* 8 Hz), 6.80 (2 H, s), and 7.2–7.4 (10 H, m).

(b) A mixture of 2,4,6-trimethylbenzoyl chloride (from 1.8 g of the acid), diphenylmethylamine (4 g), benzene (20 ml), and pyridine (1 ml) was stirred at room temperature for 18 h. Normal work-up gave a dark tarry product from which preparative t.l.c. (silica gel–ether and light petroleum) separated the amide (6b) (0.58 g, 16%) as a waxy solid with i.r. and ¹H n.m.r. spectra identical with the product of decarboxylation of (6a).

Reduction of the Adduct (5b).—A mixture of the adduct (5b) (0.4 g), ether (25 ml), and lithium aluminium hydride (0.3 g) was stirred overnight at room temperature. Normal work-up of the reaction mixture gave 2,2-diphenyl-2-(2,4,6-trimethylbenzoylamino)ethanol (6c) (0.2 g, 50%), m.p. 176–177 °C (from xylene) (Found: C, 80.0; H, 6.9; N, 3.9. C₂₄H₂₅NO₂ requires C, 80.2; H, 7.0; N, 3.9%); ν_{\max} (paste) 3 250 and 1 650 cm⁻¹; δ_{H} (CDCl₃) 2.24 (3 H, s), 2.35 (6 H, s), 4.44 (2 H, d, *J* 7 Hz), 5.50 (1 H, t, *J* 7 Hz), 6.65 (1 H, s), 6.82 (2 H, s), and 7.2–7.4 (10 H, m); treatment with D₂O removed the signal at δ 5.50 and converted the doublet at δ 4.44 into a singlet; δ_{C} (CDCl₃) 19.5 (q), 21.1 (q), 63.7, 69.6, 127.4 (d), 127.8 (d), 128.4 (d), 134.1 (s), 138.8 (s), 142.3 (s), and 171.6 (s); *m/e* 357 (1%), 341 (11), 329 (27), 196 (18), 180 (26), 176 (47), 174 (49), 147 (100), and 119 (56).

Reduction of the adduct (5b) by prolonged boiling with lithium aluminium hydride in tetrahydrofuran gave the amide (6c) as the only detectable product. The amide (6c) was recovered unchanged after attempted reduction under the same conditions.

Reaction of 2,4,6-Trimethylbenzonitrile *N*-Oxide with *t*-Butylcyanoketen.—The nitrile oxide (1 g) and the keten (from

1 g of bisazidoquinone) were boiled in dry benzene (25 ml) for 4 h. Evaporation of the solvent left an oil which on shaking with methanol (20 ml) partly crystallised giving 4-cyano-4-*t*-butyl-2-(2,4,6-trimethylphenyl)-2-oxazolin-5-one (5c) (0.8 g, 45%), m.p. 90–91 °C (from methanol) (Found: C, 71.8; H, 7.2; N, 9.9. C₁₇H₂₀N₂O₂ requires C, 71.8; H, 7.1; N, 9.9%); $\nu_{\text{max.}}$ (paste) 1 830, 1 820, and 1 660 cm⁻¹; $\lambda_{\text{max.}}$ (EtOH) 251 nm (log ϵ 3.96); δ_{H} (CDCl₃) 1.30 (9 H, s), 2.33 (3 H, s), 2.40 (6 H, s), and 6.95 (2 H, s); δ_{C} (CDCl₃) 20.5 (q), 21.3 (q), 24.6 (q), 39.9 (s), 72.8 (s), 113.4 (s), 122.2 (s), 129.3 (d), 138.1 (s), 141.9 (s), 165.4 (s), and 170.2 p.p.m. (s); *m/e* 284 (*M*⁺, 8%), 240 (C₁₆H₂₀N₂, 8), 228 (C₁₃H₁₂N₂O₂, 80), 225 (C₁₅H₁₇N₂, 72), 184 (C₁₂H₁₂N₂, 17), 183 (C₁₂H₁₁N₂, 23), 147 (C₁₀H₁₁O, 57), 146 (C₁₀H₁₂N, 33; and C₁₀H₁₀O, 35), 145 (C₁₀H₁₁N, 63), 144 (C₁₀-H₁₀N, 21), 130 (C₉H₈N, 100), and 119 (C₉H₁₁, 21).

On cooling, the methanol solution deposited methyl 2-cyano-3,3-dimethyl-2-(2,4,6-trimethylbenzoylamino)butanoate (6d) (0.7 g, 36%), m.p. 187–188 °C (from xylene) (Found: C, 68.6; H, 7.7; N, 9.1. C₁₈H₂₄N₂O₃ requires C, 68.3; H, 7.6; N, 8.9%); $\nu_{\text{max.}}$ (paste) 3 300, 3 200, 2 150, 2 220 (v. weak), 1 760, and 1 640 cm⁻¹; δ_{H} (CDCl₃) 1.18 (9 H, s), 2.26 (s) and 2.28 (s) (total 9 H), 3.89 (3 H, s), 6.23 (1 H, s), and 6.80 (2 H, s); δ_{C} (CDCl₃) 18.9 (q), 21.1 (q), 25.6 (q), 37.6 (s), 53.5 (q), 64.6 (s), 116.2 (s), 128.3 (d), 132.1 (s), 135.1 (s), 139.4 (s), 165.4 (s), and 170.3 p.p.m. (s); *m/e* 316 (*M*⁺, 1%), 260 (C₁₄H₁₆-N₂O₃, 16), 228 (C₁₃H₁₂N₂O₂, 4), 161 (C₁₁H₁₃O, 4), 147 (C₁₀-H₁₁O, 100), and 146 (C₁₀H₁₀O, 26).

Reaction of 2,4,6-Trimethylbenzotrile N-Oxide with Dimethylketen.—Dimethylketen (from 20 g of dimer) was passed into a solution of the nitrile oxide (3 g) in dry ether (100 ml) at 0 °C. After 12 h the solvent was evaporated and the residual oil (4.5 g) was separated by chromatography (silica gel and ether–light petroleum) into the following two components: 4,4-dimethyl-2-(2,4,6-trimethylphenyl)-2-oxazolin-5-one (5d) (1.5 g, 35%), m.p. 52–53 °C (from light petroleum, b.p. 60–80 °C) (Found: C, 72.4; H, 7.2; N, 6.0. C₁₄H₁₇NO₂ requires C, 72.7; H, 7.4; N, 6.1%); $\nu_{\text{max.}}$ (paste) 1 815 and 1 665 cm⁻¹; $\lambda_{\text{max.}}$ (EtOH) 235 and 265 nm (log ϵ 3.87 and 2.92); δ_{H} (CDCl₃) 1.56 (6 H, s), 2.29 (s) and 2.31 (s) (total 9 H), and 6.91 (2 H, s); δ_{C} (CDCl₃) 19.8 (q), 21.2 (q), 24.6 (q), 65.8 (s), 123.9 (s), 128.6 (d), 137.1 (s), 140.6 (s), 160.3 (s), and 181.6 p.p.m. (s); *m/e* 231 (*M*⁺, 20%), 147 (C₁₀H₁₁O, 27%), and 146 (C₁₀H₁₀O, 100%); and 4,5-dihydro-5-methyl-5-(2-methylpropanoyl)-3-(2,4,6-trimethylphenyl)isoxazole (8) (2.0 g, 39%), b.p. 134–136 °C/0.01 mmHg (Found: C, 74.5; H, 8.4; N, 5.0. C₁₇H₂₃NO₂ requires C, 74.7; H, 8.4; N, 5.1%); $\nu_{\text{max.}}$ (film) 1 715 and 1 610 cm⁻¹; δ_{H} (CDCl₃) 1.14 (3 H, d, *J* 7 Hz), 1.19 (3 H, d, *J* 7 Hz), 1.62 (3 H, s), 2.17 (6 H, s), 2.27 (3 H, s), 2.89 (1 H, d, *J* 18 Hz), 3.40 (1 H, sept, *J* 7 Hz), 3.57 (1 H, d, *J* 18 Hz), and 6.87 (2 H, s); δ_{C} (CDCl₃) 19.2, 19.6, 21.1, 23.1 (q), 35.2 (d), 47.4 (t), 90.7 (s), 125.7 (s), 128.4 (d), 136.3 (s), 138.9 (s), 158.2 (s), and 216.4 p.p.m. (s); *m/e* 273 (*M*⁺, 1%), 258 (C₁₆H₂₀NO₂, 1), 230 (C₁₅-H₂₀NO, 5), 202 (C₁₃H₁₆NO, 93), and 160 (C₁₁H₁₄N, 100).

Hydrolysis of the Oxazolinone (5d).—Alkaline hydrolysis of the adduct (5d) under conditions identical with those employed for (5b) gave 2-methyl-2-(2,4,6-trimethylbenzoylamino)propanoic acid (6e) (84%), m.p. 230–231 °C (from ethyl acetate) (Found: C, 67.2; H, 7.8; N, 5.8. C₁₄H₁₉NO₃ requires C, 67.5; H, 7.6; N, 5.6%); $\nu_{\text{max.}}$ (paste) 3 230, 3 065, 2 680, 1 710, and 1 635 cm⁻¹; δ_{H} [(CD₃)₂CO] 1.65 (6 H, s), 2.28 (s) and 2.30 (s) (total 9 H), 6.34 (2 H, s), and 7.70 (1 H, br); δ_{C} [(CD₃)₂CO] 19.0, 20.0, 25.3, 56.4, 128.4, 135.1, 136.0, 138.3, 170.0, and 175.6 p.p.m.; *m/e* 249 (*M*⁺, 12%), 147 (100), and 146 (77).

Synthesis of the Isoxazole (8).—A mixture of trimethylbenzotrile N-oxide (1.4 g), ether (20 ml), and 2,4-dimethyl-

pent-1-en-3-one (1 g) was stirred at room temperature for 2 days. Evaporation of the solvent left an oil from which preparative t.l.c. separated the adduct (8) (45%), with i.r. and ¹H n.m.r. spectra identical with the compound isolated from the reaction of the nitrile oxide with dimethylketen.

Attempted Reaction of Ketene with 2,4,6-Trimethylbenzotrile N-Oxide.—Ketene was bubbled through a solution of the nitrile oxide in ethyl acetate at room temperature for several hours. T.l.c. examination of the reaction mixture showed the presence of unchanged nitrile oxide and no other u.v. active material could be detected.

Attempted Reaction of *t*-Butylethoxycarbonylketene with 2,4,6-Trimethylbenzotrile N-Oxide.—A mixture of equimolar proportions of the nitrile oxide and *t*-butylethoxycarbonylketene²⁵ in dry benzene was boiled under reflux for 4 h. Evaporation of the solvent left an oil which on shaking with light petroleum deposited 2,4,6-trimethylphenyl isocyanate, m.p. 45 °C (lit.,²⁶ 44–45 °C); $\nu_{\text{max.}}$ (paste) 2 280 cm⁻¹; δ_{H} (CDCl₃) 2.26 (s) and 2.29 (s) (total 9 H), and 6.84 (2 H, s). T.l.c. analysis of the reaction mixture showed the presence of no other significant u.v. active material.

The isocyanate was converted by reaction with aniline in xylene into *N*-(2,4,6-trimethylphenyl)-*N'*-phenylurea, m.p. 244 °C (lit.,²⁴ 245 °C); $\nu_{\text{max.}}$ (paste) 3 280 and 1 640 cm⁻¹; identical with an authentic sample.²⁴

Attempted Reaction of Phenyl Isocyanate with 2,4,6-Trimethylbenzotrile N-Oxide.—A mixture of the nitrile oxide (1.6 g), phenyl isocyanate (1.5 g), and dry benzene (20 ml) was boiled under reflux for 24 h. T.l.c. analysis of the mixture showed that no reaction had occurred. An attempt to repeat the experiment in boiling xylene led to formation of a dark tar.

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