Ketene. Part 26.[1] The Reactions of 3,4-Dihydroisoquinoline *N*-Oxide with Ketenes, and an Attempted Synthesis of 3,4-Dihydro-3,3-dimethylquinoline *N*-Oxide

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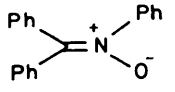
3,4-Dihydroisoquinoline *N*-oxide reacts with dimethylketene to form a 1:2 adduct (**8**) in addition to compounds (**6**) and (**7**). With cyano-t-butylketene and ethoxycarbonyl-t-butylketene the adducts (**9a**) and (**9b**) are formed. 3,3-Dimethyl-1,2,3,4-tetrahydroquinoline (**21a**) has been synthesized, but attempts to convert this into the nitrone (**20b**) were unsuccessful.

The reactions of ketenes with nitrones are known to give rise to a wide range of products, and the factors governing the choice between the various reaction pathways are only partly understood. We have recently shown that conformational factors are responsible for the difference between the reactions of *C*,*N*-diarylnitrones such as (**1**) and the analogous fluorene derivatives (**2**), which form indolones (**3**) and oxazolidinones (**4**) respectively, freedom of rotation about the N–Ph bond being essential for indolone formation.[2] We now report the results of a study of the reactions of 3,4-dihydroisoquinoline *N*-oxide (**5**) with ketenes and an attempt to synthesize a 3,4-dihydroquinoline *N*-oxide. The interest in the behaviour of (**5**) comes partly from the restricted relative orientation of the aromatic ring and the nitrone group, which are held almost co-planar, and partly from the high reactivity of (**5**) in 1,3-dipolar cycloadditions.[3] Although ketenes might formally appear to be potential dipolarophiles, cycloaddition to nitrones to form isoxazolidinones is almost unknown and there is no evidence that a normal, concerted, cycloaddition mechanism operates in the very few such cases recorded.[4]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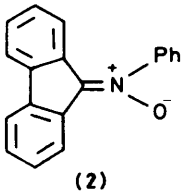
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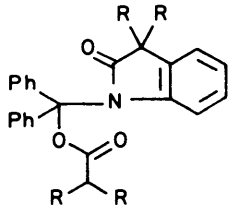
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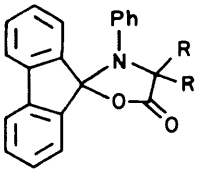
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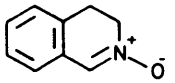
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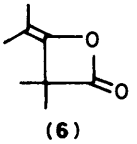
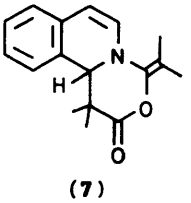

(6)

The reaction of 3,4-dihydroisoquinoline *N*-oxide (**5**) with dimethylketene in ethyl acetate at room temperature gave three products, one of which was identified as the β-lactone dimer of dimethylketene (**6**). A modest yield of the adduct of dimethylketene and isoquinoline (**7**)[5] was also obtained, and a very low yield of a 1:2 adduct of (**5**) with dimethylketene was isolated. The structure (**8**) was assigned to this compound on the basis of the spectroscopic evidence. Strong i.r. absorptions at 1 790 and 1 745 cm^{-1} indicate two carbonyl groups, the higher frequency absorption being consistent with the presence of an *O*-acyl hydroxylamino group,[6,7] and the ^{13}C n.m.r. spectrum showed two carbonyl signals at δ 169.5 and 172.4. The ^{1}H n.m.r. spectrum showed four three-proton singlets between δ 0.8 and 1.6 with other signals consistent with structure (**8**). The general pattern of spectroscopic data is closely similar to that of the dimethylketene adducts of phenanthridine and isoquinoline *N*-oxides[7] as is also the mass spectrum which shows prominent peaks at $(M-69)^+$, $(M-114)^+$, $(M-115)^+$, and $(M-155)^+$.

Compound (**5**) reacted with cyano-t-butylketene to give a 1:1 adduct in reasonable yield. In this case the spectroscopic evidence points clearly to the structure (**9a**) with a strong i.r. absorption at 1 765 cm^{-1} and a barely perceptible signal at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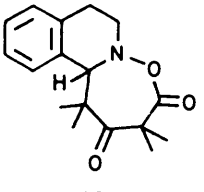
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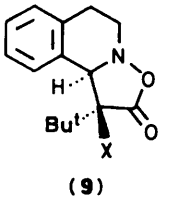
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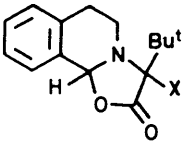
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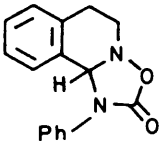
a; X = CN
b; X = CO_2Et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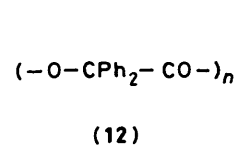
2 240 cm^{-1}. The n.m.r. spectra are also consistent with this structure, the cyano group giving a signal at δ 115.0 in the ^{13}C spectrum, in which the angular methine carbon atom absorbs at δ 63.5. The alternative structure for this adduct (**10a**), which might have been expected by analogy with a number of other ketene-nitrone[8] and ketene-nitrile oxide[9] adducts, would be expected to show an n.m.r. signal due to the angular methine carbon atom at significantly higher frequency. The corresponding signal in the spectrum of the adduct (**11**) of (**5**) with phenyl isocyanate[10] is at δ 78.0. The most convincing evidence for the *iso*xazolidinone structure (**9a**) comes from the mass spectrum in which the base peak (*m/z* 147) corresponds to the molecular ion of (**5**) and there is no significant peak at higher *m/z* observed (apart from 148^+). This fragmentation is identical with that observed for other adducts of cyano-t-butylketene with nitrones for which isoxazolidinone structures have been established,[4] and quite different from that expected for structure (**10a**).[8] Additional evidence for the presence of an N–O bond in this adduct comes from the natural abundance ^{15}N n.m.r. spectrum, which shows an absorption at δ −188.5, close to that observed for the N(2) resonance (δ −193 to −199) in a series of 1,2,4-oxadiazolidinones (nitrone-isocyanate adducts) like (**11**).[11] The observation of a nuclear Overhauser effect establishes the stereochemistry shown in (**9**), excitation of the angular methine proton giving a small (1%) enhancement of the t-butyl signal, whilst excitation of the t-butyl protons gives a large (19%) enhancement of the angular methine proton signal. In both cases a 2% enhancement of an aromatic proton signal is also observed.

The reaction of (**5**) with ethoxycarbonyl-t-butylketene also gave a 1:1 adduct to which structure (**9b**) is assigned on the basis of spectroscopic evidence similar to that adduced for structure (**9a**) and, in particular, a ^{15}N n.m.r. chemical shift of δ −192.5. This seems to be the first adduct of this type observed for this ketene. In those previously reported cases where cyano-t-butylketene gives isoxazolidinone adducts[4] the ethoxycarbonylketene does not form cyclo adducts but reacts by a different pathway. An n.m.r. n.O.e. difference measurement showed enhancement of the t-butyl signal (3%) on excitation of the angular proton, and enhancement of the proton signal (13%) on excitation of the t-butyl methyl groups. In both experiments some enhancement of aromatic signals was observed but there were no other significant effects. Excitation of the ester methyl group had no significant effect on the signals due to the proton at the ring junction or the aromatic protons and only trivial effects on the signals between δ 2.8 and 3.7. On this basis we assign the stereochemistry shown in (**9b**).

The reaction of diphenylketene with (**5**) in boiling benzene gave the polyester of benzilic acid (**12**) as the only identifiable product. No reaction could be detected between ketene and (**5**) in ethyl acetate at room temperature, t.l.c. analysis of the reaction mixture showed the nitrone to be unchanged after a prolonged period.

The formation of (**8**), (**9a**), and (**9b**) appears to proceed in all cases *via* a zwitterion of part-structure (**13**), which in the case of the cyano- and ethoxycarbonyl-ketene reactions can cyclise to give the observed products. Why the rearrangement to give adducts of structure (**10**), observed in a number of other ketene-nitrone cycloadditions, does not occur in these cases is unclear. The corresponding intermediate (**13a**) formed from (**5**) and diphenylketene very probably decomposes to form an α-lactone which polymerises to give the polyester (**12**).

To explain the formation of a substantial proportion of (**7**) from the reaction of dimethylketene with (**5**), we propose that the zwitterion (**13b**) forms (**14**) by intramolecular proton abstraction. A Stevens rearrangement could then give the dihydroisoquinoline (**15**), which would eliminate isobutyric acid to form isoquinoline, which was detected in the reaction mixture



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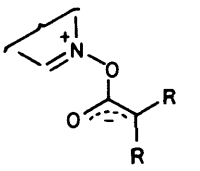
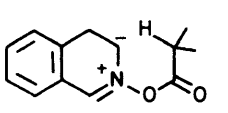


(13) a; R = Ph
b; R = Me



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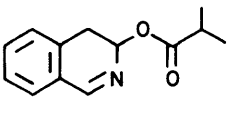

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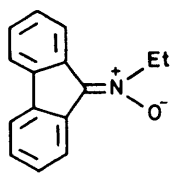

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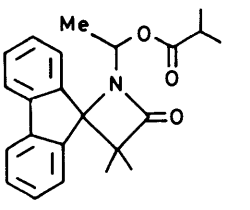

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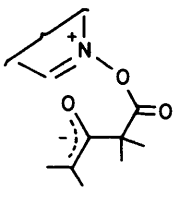

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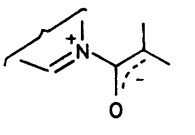


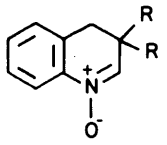
(19)

by t.l.c. Subsequent addition of dimethylketene to isoquinoline would form (**7**). A reaction sequence similar to (**13**) ⟶ (**15**) is probably involved in the reaction of dimethylketene with nitrone (**16**) to form (**17**).[8b] The minor product (**8**) of the reaction of (**5**) with dimethylketene could be formed by acylation of (**13b**) by more dimethylketene to form (**18**) followed by cyclisation. This is the third time that *C*-acylation of enolates (**13**) formed from *N*-oxides and ketenes has been observed,[7,9] rather than the *O*-acylation of zwitterions of type (**19**) commonly observed in the formation of adducts like (**7**). Intramolecular acylation of the enolate anion in the zwitterion (**18**) is probably the source of the dimethylketene dimer (**6**).

The interest in (**5**) arising from the fixed spatial relationship of the aromatic ring and the nitrone function extends also to the corresponding 3,4-dihydroquinoline *N*-oxide (**20a**), particularly since the formation of indolones such as (**3**) depends on a [3,3] migration involving the *N*-aryl group.[2,12] The unsubstituted dihydroquinoline *N*-oxide (**20a**) is not expected to be stable since tautomerisation and elimination of water would form quinoline. We have therefore attempted a synthesis of the 3,3-dimethyl derivative (**20b**). The plan was to synthesize 3,3-dimethyltetrahydroquinoline (**21a**) and then convert this into (**20b**) by a procedure already successfully employed in a dihydroisoquinoline *N*-oxide synthesis.

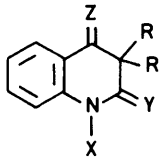
The first attempt at synthesis of (**21a**) was based on dimethylation of the *N*-tosyl dihydroquinolone (**21b**). The phenylamino ester (**22a**)[13] can be converted by standard procedures *via* (**22b**) and (**22c**) into (**21b**).[14]

Attempts to alkylate (**21b**) under strongly basic conditions were mostly unsuccessful and it appears that the enolate anion of (**21b**) decomposes rapidly by β-elimination. Only by the slow



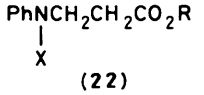
(20)

a; R = H
b; R = Me



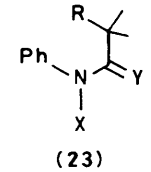
(21)

	R	X	Y	Z
a;	Me	H	H_2	H_2
b;	H	Tosyl	H_2	O
c;	Me	Tosyl	H_2	O
d;	Me	Tosyl	H_2	H_2
e;	Me	OH	H_2	H_2
f;	Me	CH_2CH_2CN	H_2	H_2
g;	Me	Et	H_2	H_2
h;	Me	OH	O	H_2
i;	Me	H	O	H_2
j;	Me	H	O	O



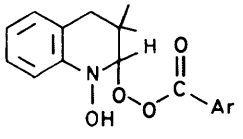
(22)

	R	X
a;	Me	H
b;	Me	Tosyl
c;	H	Tosyl



(23)

	R	X	Y
a;	CO_2H	H	O
b;	CH_2OH	H	H_2
c;	CH_2OH	Tosyl	H_2
d;	CH_2OAc	Tosyl	H_2
e;	CO_2H	Tosyl	H_2
f;	$CH_2OTosyl$	Tosyl	H_2
g;	$CH_2OTosyl$	H	O



(24)

addition of potassium t-butoxide to a solution of (**21b**) in a large excess of neat methyl iodide was it possible to obtain a low yield of (**21c**). At this stage this approach was abandoned.

A second, successful synthesis of (**21a**) started with the mono-anilide of dimethylmalonic acid (**23a**). Reduction to (**23b**) and partial tosylation gave (**23c**). That tosylation had occurred on nitrogen was confirmed by acetylation of (**23c**) to give (**23d**) which showed i.r. absorption at 1 740 cm^{-1}. Oxidation of (**23c**) to (**23e**) and ring closure gave (**21c**), identical with the product of methylation of (**21b**). Wolff-Kishner reduction of (**21c**) gave (**21d**) which was reductively converted into (**21a**) in overall yield of 41% from (**23a**).

Several unsuccessful attempts were made to convert the amine (**21a**) into the nitrone (**20b**). Attempts to oxidise (**21a**) directly to the *N*-hydroxy derivative (**21e**) with hydrogen peroxide or *m*-chloroperoxybenzoic acid gave dark intractable tars. Thesing and Mayer[15] have reported the conversion of tetrahydroisoquinoline to the *N*-hydroxy derivative by reaction with ethyl acrylate and *N*-oxidation of the resulting tertiary amine, followed by Cope elimination of ethyl acrylate. The *N*-hydroxy tetrahydroisoquinoline was then oxidised to (**5**) by mercuric oxide. We were unable to add the amine (**21a**) to ethyl acrylate, but addition of acrylonitrile gave (**21f**) and alkylation with ethyl iodide gave (**21g**). Oxidation of (**21f**) with *m*-chloroperoxybenzoic acid proceeded very slowly, and the only products isolated were identified by their spectroscopic properties as (**21h**) and (**21i**). Compound (**21h**) was also produced by the oxidation of (**21a**) with sodium tungstate and hydrogen peroxide.[16] The structure (**21i**) was confirmed by a synthesis in which (**23a**) was cyclised by phosphorus pentaoxide in boiling xylene to give (**21j**) which was catalytically reduced to (**21i**). The amide (**21i**) was not further oxidised to (**21h**) by peracid. At this stage the attempt to synthesise (**20b**) was abandoned.

The conversion of (**21f**) into (**21h, i**) was quite unexpected in view of Thesing's previous work.[15] We suggest that *N*-oxidation of (**21f**) gives the desired *N*-oxide but is followed by a rapid Cope elimination, possibly accelerated by steric compression, forming the *N*-hydroxy compound (**21e**), which undergoes oxidation by the peracid to form (**20b**). Subsequent addition of percarboxylic acid to the nitrone function to give (**24**) could be followed by either an elimination of water giving the percarboxylic ester of the enol of (**21i**), subsequently hydrolysed to the amide, or an intramolecular elimination ('ester pyrolysis') of carboxylic acid, facilitated by the easy cleavage of the weak O–O bond, to form (**21h**).

Experimental

N.m.r. spectra were measured with Perkin-Elmer R34 (220 MHz), Bruker AM250, and JEOL PFT-100 spectrometers. The natural abundance ^{15}N n.m.r. spectra were recorded at 25.4 MHz on the Bruker AM250 spectrometer using 10-mm sample tubes. Samples were dissolved in 0.1M $MeNO_2$ in deuteriochloroform containing 0.1M [$Cr(acac)_3$] relaxation reagent. Spectra were measured with proton decoupling and suppression of n.O.e. using a delay time of 3 s, chemical shifts are with respect to $MeNO_2$. Mass spectra were measured with Kratos MS25 and MS80 spectrometers. Dimethylketene was prepared by pyrolysis of tetramethylcyclobutanedione,[17] cyano-t-butylketene,[18] ethoxycarbonyl-t-butylketene,[4b,19] and 3,4-dihydroquinoline *N*-oxide[20] were prepared by published procedures. Ether refers to diethyl ether and light petroleum to the fraction b.p. 60—80 °C.

Reaction of 3,4-*Dihydroisoquinoline* N-*Oxide* (**5**) *with Dimethylketene.*—Dimethylketene (from 20 g of dimer) was passed into a solution of (**5**) (2 g) in dry ethyl acetate (100 ml). After 12 h at room temperature the solvent was evaporated and the residual oil separated by column chromatography (silica gel and light petroleum–ether) into the following components: (i) the β-lactone (**6**) (3.5 g, 18%), b.p. 160—170 °C (lit.,[21] 165—175 °C); (ii) the dimethylketene-isoquinoline adduct (**7**) (0.6 g, 17%), m.p. 106 °C (lit.,[5] 106 °C), $\delta_C(CDCl_3)$ 16.3 (q), 17.6 (q), 20.1 (q), 22.1 (q), 48.8 (s), 60.6 (d), 99.5 (d), 101.2 (s), 123.8, 124.1, 125.2, 127.9, 128.4, 133.0, 133.7, 141.5 (s), and 173.1 (s); and (iii) 1,7,8,12b-*Tetrahydro*-1,1,3,3-*tetramethyl*[1,2]*oxazepino*[3,2-a]-*isoquinoline*-2,4(3H)-*dione* (**8**) (0.1 g, 3%), m.p. 158 °C (from benzene and light petroleum) (Found: C, 71.2; H, 7.5; N, 4.7. $C_{17}H_{21}NO_3$ requires C, 71.1; H, 7.4; N, 4.9%); $\nu_{max.}$(paste) 1 790 and 1 745 cm^{-1}; $\delta_H(CDCl_3)$ 0.80 (3 H, s), 1.35 (3 H, s), 1.40 (3 H, s), 1.55 (3 H, s), 2.4—2.6 (1 H, m), 2.7—2.85 (1 H, m), 2.9—3.2 (2 H, m), 3.88 (1 H, s), 6.9—7.1 (1 H, br d, *J* 8 Hz), and 7.15—7.3 (3 H, m); $\delta_C(CDCl_3)$ 16.0 (q), 18.3 (q), 24.8 (q), 26.3 (q), 29.5 (t), 40.0 (t), 56.5 (s), 65.4 (d), 68.9 (s), 126.4 (d), 126.7 (d), 127.5 (d), 128.0 (d), 132.3 (s), 136.8 (s), 169.5 (s), and 172.4 (s); *m/z* 287 (M^+, 10%), 218 ($C_{13}H_{16}NO_2$, 85), 173 ($C_{12}H_{15}N$, 93), 172

($C_{12}H_{14}N$, 53), 158 ($C_8H_{14}O_3$, 25), 132 ($C_9H_{10}N$, 67), 131 (C_9H_9N, 50), and 117 (100). Compounds (**6**) and (**7**) were identified by i.r. and ^1H n.m.r. comparison with authentic samples.

When this reaction was performed in benzene, isoquinoline was detected in the crude reaction mixture by t.l.c.

Reaction of the N-*Oxide* (**5**) *with Cyano-t-butylketene.*—A mixture of the *N*-oxide (**5**) (1 g), cyano-t-butylketene (from 1 g of the bisazidoquinone), and dry benzene (35 ml) was boiled for 30 min. Evaporation of the solvent left an oil which crystallised on shaking with light petroleum giving 1-*cyano*-1-*t*-*butyl*-1,5,6,10b-*tetrahydroisoxazolo*[3,2-a]*isoquinolin*-2-*one* (**9a**) (0.95 g, 51%), m.p. 148—149 °C (from ethanol) (Found: C, 71.1; H, 6.7; N, 10.6. $C_{16}H_{18}N_2O_2$ requires C, 71.1; H, 6.7; N, 10.4%); $\nu_{max.}$(paste) 2 240vw and 1 765 cm^{-1}; $\delta_H(CDCl_3)$ 1.43 (9 H, s), 2.51 (1 H, br d, *J* 15 Hz), 2.9—3.3 (2 H, m), 3.9—4.05 (1 H, br d, *J* 15 Hz), 5.17 (1 H, s), and 7.1—7.4 (4 H, m); $\delta_C(CDCl_3)$ 21.6 (t), 26.4 (q), 39.2 (s), 50.9 (t), 63.5 (s), 65.4 (d), 115.0 (s), 126.9, 128.1, 128.6, 128.8, 129.4, 134.8 (s), and 168.2 (s); $\delta_N(CDCl_3)$ −112.6 (CN) and −188.5 (N–O); *m/z* 270 (M^+, 3%), 255 (3), 148 (35), 147 (100), and 131 (40).

Reaction of the N-*Oxide* (**5**) *with Ethoxycarbonyl-t-butylketene.*—A mixture of the *N*-oxide (**5**) (1.3 g), the ketene (1.5 g), and dry benzene (70 ml) was boiled for 6 h. Evaporation of the solvent left an oil which, on shaking with light petroleum, deposited 1-*ethoxycarbonyl*-1-*t*-*butyl*-1,5,6,10b-*tetrahydroisoxazolo*[3,2-a]*isoquinolin*-2-*one* (**9b**) (0.9 g, 32%), m.p. 114 °C (from light petroleum) (Found: C, 68.2; H, 7.5; N, 4.2. $C_{18}H_{23}NO_4$ requires C, 68.1; H, 7.3; N, 4.4%); $\nu_{max.}$(paste) 1 760 and 1 740 cm^{-1}; $\delta_H(CDCl_3)$ 0.73 (3 H, t, *J* 8 Hz), 1.40 (9 H, s), 2.4—2.55 (1 H, br d, *J* 15 Hz), 2.85—3.3 (3 H, m), 3.5—3.7 (1 H, m), 3.8—4.0 (1 H, br d, *J* 15 Hz), 5.35 (1 H, s), 6.9—7.0 (1 H, m), and 7.0—7.3 (3 H, m); $\delta_C(CDCl_3)$ 13.1 (q), 22.9 (t), 26.4 (q), 36.9 (s), 51.9 (t), 61.2 (t), 66.6 (d), 70.3 (s), 126.5, 127.0, 127.2, 132.4 (s), 137.0 (s), 166.4 (s), and 172.7 (s); $\delta_N(CDCl_3)$ −192.5; *m/z* 317 (M^+, 2%), 272 (4), 214 (4), 155 (10), 148 (50), and 147 (100).

Reaction of the N-*Oxide* (**5**) *with Diphenylketene.*—The *N*-oxide (**5**) (1 g) and diphenylketene (from 3 g of diazoketone) were boiled in dry benzene (25 ml) under nitrogen for 2 h. Addition of light petroleum deposited a white solid identified as the polyester of benzilic acid (**12**) (1.5 g, 57%) by i.r. comparison with an authentic sample.[22]

The 3,4-*Dihydroisoquinoline–Phenyl Isocyanate Adduct* (**11**).—This adduct was prepared by the recorded method;[10] $\nu_{max.}$(paste) 1 785 cm^{-1}; $\delta_H(CDCl_3)$ 3.0—3.15 (2 H, m), 3.5—3.75 (2 H, m), 6.15 (1 H, s), 6.49 (1 H, d, *J* 8 Hz), 6.9—7.1 (3 H, m), and 7.15—7.4 (6 H, m); $\delta_C(CDCl_3)$ 26.9 (t), 49.8 (t), 78.0 (d), 126.0, 128.2, 128.3, 129.3, 129.4, 134.7 (s), and 156.8 (s).

Dimethylmalonic Acid.—2,2-Dimethylpropane-1,3-diol (50 g) was added in small portions to ice-cooled concentrated nitric acid (300 ml) with stirring, the temperature being maintained below 35 °C. The mixture was left overnight and then most of the nitric acid and water was evaporated under reduced pressure (temp. < 70 °C). The residue was chilled and the dimethylmalonic acid collected (51 g, 82%), m.p. 193 °C (from water).

Preparation of the Anilide (**23a**).—A mixture of finely powdered dimethylmalonic acid (13 g), dry tetrahydrofuran (40 ml), and thionyl chloride (14.7 g, 9.1 ml) was boiled for 2 h and, after cooling, added slowly with stirring to an ice-cooled solution of aniline (19 g) in ether (40 ml). The solvents were evaporated and the residue was washed with dilute hydrochloric acid and extracted with dichloromethane (2 × 50 ml). The solution was extracted twice with dilute sodium hydroxide and the aqueous extract was acidified with hydrochloric acid to precipitate the anilide (**23a**) (13.5 g, 67%), m.p. 133 °C (from aqueous ethanol) (lit.,[23] 133 °C); $\nu_{max.}$(paste) 3 320, 1 710, 1 650, and 1 600 cm^{-1}; $\delta_H(CDCl_3)$ 1.60 (6 H, s), 7.09 (1 H, t, *J* 8 Hz), 7.30 (2 H, t, *J* 8 Hz), 7.55 (2 H, d, *J* 8 Hz), 8.2 (1 H, br), and 8.9 (1 H, br); $\delta_C[(CD_3)_2CO]$ 23.8, 51.2, 120.9, 124.4, 129.3, 139.8, 171.3, and 175.5.

N-(2,2-*Dimethyl*-3-*hydroxypropyl*)-N-*phenyltoluene*-p-*sulphonamide* (**23c**).—A solution of the anilide (**23a**) (21.8 g) in tetrahydrofuran (200 ml) was added slowly with stirring to an ice-cooled slurry of lithium aluminium hydride (14 g) in tetrahydrofuran (200 ml). The mixture was boiled under nitrogen for 18 h and the excess of hydride was decomposed by cautious addition of water. The mixture was filtered and the filtrate evaporated. The residue was dissolved in ether and the ether solution was washed with dilute aqueous sodium hydroxide and water, dried ($MgSO_4$), and evaporated to leave the crude *hydroxy amine* (**23b**) as an oil; $\nu_{max.}$(film) 3 400 cm^{-1}; $\delta_H(CDCl_3)$ 0.93 (6 H, s), 2.96 (2 H, s), 3.3 (2 H, br, removed by D_2O treatment), 3.4 (2 H, s), 6.5—6.7 (3 H, m), and 7.05—7.2 (2 H, m); $\delta_C(CDCl_3)$, 22.8 (q), 36.0 (s), 53.1 (t), 71.1 (t), 113.2, 117.5, 129.2, and 148.8.

The crude material was dissolved in pyridine (90 ml) and the solution cooled to 0 °C. A solution of toluene-*p*-sulphonyl chloride (16.1 g) in chloroform (110 ml) was then added slowly with stirring and the mixture left overnight at 0 °C. Standard work-up of the mixture gave the *sulphonamide* (**23c**) (30.2 g, 86%), m.p. 84—86 °C (from light petroleum) (Found: C, 65.0; H, 7.1; N, 3.8. $C_{18}H_{23}NO_3S$ requires C, 64.9; H, 6.9; N, 4.2%; $\nu_{max.}$ 3 520 and 3 370 cm^{-1}; $\delta_H(CDCl_3)$ 0.71 (6 H, s), 2.40 (3 H, s), 3.43 (2 H, s), 3.48 (2 H, s), 7.05—7.15 (2 H, m), 7.20—7.35 (5 H, m), and 7.40 (2 H, d, *J* 8 Hz); $\delta_C(CDCl_3)$ 21.5, 23.1 (q), 38.5 (s), 60.0 (t), 67.7 (t), 127.7, 128.9, 129.3, 134.3 (s), 141.5 (s), and 143.6 (s).

During the course of several preparations of (**23c**) the following two by-products were also isolated: N-(2,2-*dimethyl*-3-p-*tolylsulphonyloxypropyl*)-N-*phenyltoluene*-p-*sulphonamide* (**23f**), m.p. 163—164 °C (from ethanol) (Found: C,61.4; H, 5.8; N, 2.9; S, 13.4. $C_{25}H_{29}NO_5S_2$ requires C, 61.6; H, 6.0; N, 2.9; S, 13.2%); $\delta_H(CDCl_3)$ 0.89 (6 H, s) 2.40 (3 H, s), 2.45 (3 H, s), 3.50 (2 H, s), 3.60 (2 H, s), 7.0—7.1 (2 H, m), 7.15—7.4 (9 H, m), and 7.63 (2 H, d, *J* 8 Hz); $\delta_C(CDCl_3)$ 21.5 (q), 22.7 (q), 37.0 (s), 56.8 (t), 76.0 (t), and 127.6—143.4; and 2,2-*dimethyl*-N-*phenyl*-3-p-*tolylsulphonyloxypropionamide* (23 g), m.p. 125—126 °C (from benzene–light petroleum) (Found: C, 62.4; H, 6.1; N, 3.9; S, 9.5. $C_{18}H_{21}NO_4S$ requires C, 62.2; H, 6.1; N, 4.0; S, 9.2%); $\nu_{max.}$(paste) 3 390 and 1 690 cm^{-1}; $\delta_H(CDCl_3)$ 1.27 (6 H, s), 2.4 (3 H, s), 4.08 (2 H, s), 7.05—7.15 (1 H, m), 7.25—7.35 (4 H, m), 7.45 (2 H, d, *J* 8 Hz), 7.57 (1 H, br), and 7.74 (2 H, d, *J* 8 Hz); $\delta_C(CDCl_3)$ 21.6 (q), 22.3 (q), 43.3 (s), 75.4 (t), 120.2 (d), 124.5 (d), 127.9 (d), 128.8 (d), 129.9 (d), 132.2 (s), 137.4 (s), 145.0 (s), and 172.3 (s); *m/z* 347 (M^+, 80%) and 227 (43).

N-(3-*Acetoxy*-2,2-*dimethylpropyl*)-N-*phenyltoluene*-p-*sulphonamide* (**23d**).—A mixture of compound (**23c**) (1.5 g), pyridine (9 ml), and acetic anhydride (0.5 ml) was left at room temperature overnight. Standard work-up gave compound (**23d**) (1.43 g, 85%), m.p. 82 °C (from aqueous ethanol) (Found: C, 64.2; H, 6.7; N, 3.8. $C_{20}H_{25}NO_4S$ requires C, 64.0; H, 6.7; N, 3.7%); $\nu_{max.}$(paste) 1 740 cm^{-1}; $\delta_H(CDCl_3)$ 0.94 (6 H, s), 1.82 (3 H, s), 2.40 (3 H, s), 3.52 (2 H, s), 3.65 (2 H, s), 7.0—7.1 (2 H, m), 7.15—7.3 (5 H, m), and 7.37 (2 H, d, *J* 8 Hz); $\delta_C(CDCl_3)$ 20.5 (q), 21.5 (q), 23.2 (q), 36.5 (s), 57.1 (t), 69.9 (t), 127.7, 127.8, 128.9, 129.2, 135.2 (s), 141.2 (s), 143.2 (s), and 170.4 (s).

Oxidation of Compound (**23c**).—A mixture of concentrated

sulphuric acid (8 ml) and water (5 ml) was added to a solution of compound (**23c**) (23 g) in acetic acid (150 ml) and this mixture was added slowly with stirring to a hot (60 °C) solution of sodium dichromate (11.6 g) in water (30 ml) at a rate which controlled the vigorous reaction. The reaction mixture was then boiled for 2 h, diluted with water (100 ml), and chilled. The solid product was collected and washed with dilute hydrochloric acid and water to leave 3-(N-*phenyl*-p-*tolylsulphonyl*-3-*amino*)-2,2-*dimethylpropionic acid* (**23e**) (20.8 g, 87%), m.p. 182 °C (from aqueous acetic acid) (Found: C, 61.5; H, 6.0; N, 4.4. $C_{18}H_{21}NO_4S$ requires C, 62.2; H, 6.0; N, 4.0%); $\nu_{max.}$(paste) 3 500—2 600br, 1 710 and 1 695 cm^{-1}; $\delta_H(CDCl_3)$ 1.17 (6 H, s), 2.40 (3 H, s), 3.89 (2 H, s), 7.0—7.1 (2 H, m), 7.2—7.3 (3 H, m), 7.32 (2 H, d, *J* 8 Hz), and 7.42 (2 H, d, *J* 8 Hz); $\delta_C[(CD_3)_2CO]$ 21.4, 24.0, 43.8, 58.8, 128.4, 129.2, 130.1, 136.6, 141.2, 144.2, and 177.2.

This oxidation was also performed by addition of powdered potassium permanganate (0.7 g) to a solution of compound (**23c**) (1 g) in acetone (20 ml) at room temperature and stirring the mixture overnight. This procedure proved unreliable when the scale of the preparation was increased.

3,3-*Dimethyl*-1,2-*dihydro*-1-p-*tolylsulphonylquinolin*-4(3H)-*one* (**21c**).—(*a*) A solution of the carboxylic acid (**23e**) (8 g) in xylene (250 ml) was boiled with phosphorus pentaoxide (10 g) for 2 h. The xylene solution was decanted and evaporated to leave the *quinolone* (**21c**) (4.9 g, 65%), m.p. 148 °C (from aqueous ethanol) (Found: C, 65.5; H, 5.9; N, 4.1; S, 10.0. $C_{18}H_{19}NO_3S$ requires C, 65.6; H, 5.8; N, 4.2; S, 9.7%); $\nu_{max.}$(paste) 1 690 cm^{-1}; $\delta_H(CDCl_3)$ 1.27 (6 H, s), 2.42 (3 H, s), 3.98 (2 H, s), 7.10 (1 H, t, *J* 8 Hz), 7.33 (2 H, d, *J* 8 Hz), 7.41 (1 H, t, *J* 8 Hz), 7.63 (1 H, d, *J* 8 Hz), 7.81 (2 H, d, *J* 8 Hz), and 8.02 (1 H, d, *J* 8 Hz); $\delta_C(CDCl_3)$ 21.6 (q), 42.6 (s), 57.2 (t), 118.5 (d), 121.8, 123.3, 126.8, 129.0, 130.0, 134.4 (d), 137.0 (s), 142.2 (s), 144.3 (s), and 197.7 (s); *m/z* 329 (M^+, 30%) and 273 (30).

(*b*) A solution of potassium (1 g) in t-butyl alcohol (30 ml) was added dropwise with stirring to an ice-cooled solution of the quinolone (**21b**)[14] (2 g) in methyl iodide (20 ml). After the mixture had been stirred at 0 °C for 10 min, water (20 ml) was added and the methyl iodide evaporated; the residue was then extracted with ethyl acetate (2 × 50 ml). The organic extract was dried ($MgSO_4$) and evaporated to leave an oil which crystallised when shaken with methanol to give the *quinolone* (**21c**) (0.5 g, 23%), identical with the product of the previous preparation.

3,3-*Dimethyl*-1,2,3,4-*tetrahydro-p-tolylsulphonylquinoline* (**21d**).—A mixture of compound (**21c**) (5 g), hydrazine hydrate (100%: 50 g), hydrazine dihydrochloride (13 g), and diethylene glycol (350 ml) was boiled for 12 h. Potassium hydroxide (18.7 g) was added and the mixture distilled slowly under nitrogen until the pot temperature reached 210 °C. After being boiled under reflux under nitrogen for a further 12 h the mixture was cooled and extracted with ether (3 × 100 ml). The ethereal extracts were washed with water, dried ($MgSO_4$), and evaporated to leave the *title compound* (**21d**) (4.3 g, 90%), m.p. 91 °C (from light petroleum) (Found: C, 68.8; H, 6.7; N, 4.4; S, 10.3. $C_{18}H_{21}NO_2S$ requires C, 68.5; H, 6.7; N, 4.4; S, 10.2%); $\delta_H(CDCl_3)$ 1.01 (6 H, s), 2.49 (5 H, s), 3.60 (2 H, s), 6.9—7.1 (3 H, m), 7.23 (2 H, d, *J* 8 Hz), 7.61 (1 H, d, *J* 8 Hz), and 7.69 (2 H, d, *J* 8 Hz); $\delta_C(CDCl_3)$ 21.5 (q), 26.5 (q), 30.3 (s), 41.6 (t), 57.4 (t), 120.3 (d), 123.4 (d), 126.4, 126.8, 127.5, 129.6, 129.8, 136.1 (s), 137.5 (s), and 143.4 (s); *m/z* 315 (M^+, 45%).

A small amount of the *azine* of compound (**21c**) was formed as a by-product of the hydrazone formation and was obtained as yellow crystals, m.p. 227 °C (from acetic acid) (Found: C, 65.7; H, 5.9; N, 8.4. $C_{36}H_{38}N_4O_4S_2$ requires C, 66.0; H, 5.9; N, 8.6%); *m/z* 654 (M^+).

3,3-*Dimethyl*-1,2,3,4-*tetrahydroquinoline* (**21a**).—A mixture of 1,2-dimethoxyethane (120 ml), sodium (2 g), and naphthalene (11 g) was stirred under nitrogen for 1 h, and a solution of compound (**21d**) (4.3 g) in a small volume of 1,2-dimethoxyethane was added. After the mixture had been stirred at room temperature for 1 h water (50 ml) was added and the mixture was extracted with ether (2 × 100 ml). The ether extract was washed several times with dilute hydrochloric acid and the combined acidic extracts were washed once with ether and then neutralised with ammonia. Ether extraction and standard work-up gave the *amine* (**21a**) as an oil (2.1 g, 95%), b.p. 120—125 °C/1.5 mmHg; $\nu_{max.}$(film) 3 420 cm^{-1}; $\delta_H(CDCl_3)$ 1.00 (6 H, s), 2.48 (2 H, s), 2.89 (2 H, s), 3.78 (1 H, br), 6.47 (1 H, d, *J* 8 Hz), 6.60 (1 H, t, *J* 8 Hz), and 6.85—7.05 (2 H, m); $\delta_C(CDCl_3)$ 26.4 (CH_3), 27.9 (C), 41.1 (CH_2), 53.1 (CH_2), 113.5 (CH), 116.7 (CH), 120.4 (C), 126.5 (CH), 129.8 (CH), and 143.3 (C); *m/z* 161 (M^+, 100%). The N-*benzoyl derivative* was obtained as an oil, b.p. 166—172 °C/0.01 mmHg (Found: C, 81.4; H, 7.5; N, 5.1. $C_{18}H_{19}NO$ requires C, 81.5; N, 7.2; N, 5.3%); $\nu_{max.}$(film) 1 720w and 1 640 cm^{-1}; $\delta_H(CDCl_3)$ 1.06 (6 H, s), 2.70 (2 H, s), 3.62 (2 H, s), 6.8—7.2 (4 H, m), and 7.2—7.5 (5 H, m); $\delta_C(CDCl_3)$ 26.9, 31.7, 41.7, 56.1, 124.3, 124.7, 125.3, 128.1, 128.4, 128.8, 129.4, 130.2, 136.4, 137.9, and 170.5; *m/z* 265 (M^+, 55%) and 105 (100).

(*b*) Sodium (7 g) was added slowly in small pieces to a suspension of compound (**21d**) (3 g) in boiling butan-1-ol (100 ml). After all the sodium had reacted, water (100 ml) was added to the mixture and the butanol solution was separated and extracted several times with dilute hydrochloric acid. The acidic extracts were extracted with ether (3 × 50 ml) and then neutralised with ammonia. Ether extraction and standard work-up of the ethereal solution gave the amine (**21a**) (1.1 g, 70%).

1-*Ethyl*-3,3-*dimethyl*-1,2,3,4-*tetrahydroquinoline* (**21g**).—A mixture of the amine (**21a**) (1.3 g), ethyl iodide (4 g), acetonitrile (10 ml), and potassium carbonate (2 g) was stirred at room temperature for 4 days, by which time the starting material had disappeared. Preparative t.l.c. (silica gel, light petroleum–ether, 9:1) separated the *tertiary amine* (**21g**) (1.2 g, 79%) as an oil, b.p. 120—130 °C/2 mmHg (Found: C, 84.5; H, 10.1; N, 7.2. $C_{13}H_{19}N$ requires C, 84.5; H, 10.1; N, 7.4%); $\delta_H(CDCl_3)$ 0.95 (6 H, s), 1.09 (3 H, t, *J* 7 Hz), 2.45 (2 H, s), 2.85 (2 H, s), 3.31 (2 H, q, *J* 7 Hz), 6.45—6.6 (2 H, m), 6.88 (1 H, d, *J* 8 Hz), and 7.01 (1 H, t, *J* 8 Hz); *m/z* 189 (M^+, 40%) and 174 (100).

1-(2-*Cyanoethyl*)-3,3-*dimethyl*-1,2,3,4-*tetrahydroquinoline* (**21f**).—A mixture of the crude amine (**21a**) [from reduction (*a*) of 3 g of the tosyl derivative (**21d**)], acetic acid (10 ml), and acrylonitrile (4 g) was boiled for 18 h. The mixture was neutralised with aqueous sodium carbonate and extracted with chloroform (50 ml). Evaporation of the dried ($MgSO_4$) chloroform extract left an oil from which column chromatography (silica gel, light petroleum–ether, 4:1) separated the *cyanoethyl amine* (**21f**) (1.7 g, 85%) as an oil, b.p. 180—185 °C/2 mmHg (Found: C, 78.7; H, 8.4; N, 13.3. $C_{14}H_{18}N_2$ requires C, 78.5; H, 8.5; N, 13.1%); $\nu_{max.}$(film) 2 250 cm^{-1}; $\delta_H(CDCl_3)$ 1.00 (6 H, s), 2.50 (2 H, s), 2.58 (2 H, t, *J* 7 Hz), 3.00 (2 H, s), 3.65 (2 H, t, *J* 7 Hz), 6.48 (1 H, d, *J* 8 Hz), 6.63 (1 H, t, *J* 8 Hz), 6.95 (1 H, d, *J* 8 Hz), and 7.07 (1 H, t, *J* 8 Hz); $\delta_C(CDCl_3)$ 14.9 (CH_2), 26.3 (CH_3), 28.1 (C), 41.7 (CH_2), 47.4 (CH_2), 61.2 (CH_2), 109.4 (CH), 116.9 (CH), 118.4 (CN), 121.8 (C), 127.0 (CH), 130.1 (CH), and 142.1 (C); *m/z* 214 (M^+, 25%) and 174 (100).

Peracid Oxidation of Compound (**21f**).—*m*-Chloroperoxybenzoic acid (12 g) was added to a solution of the cyanoethyl amine (**21f**) (3 g) in dry ether (100 ml) and the mixture was set aside for 4 days, by which time the starting material was no

longer present. The ether was evaporated and the residue dissolved in chloroform and this solution was washed with saturated aqueous sodium hydrogencarbonate and water and then dried ($MgSO_4$). The chloroform was evaporated and column chromatography (silica gel, light petroleum–ether, 1:1) of the residue separated the following two compounds. (i) 1-*Hydroxy*-3,3-*dimethyl*-3,4-*dihydroquinolin*-2(1H)-*one* (**21h**) (0.54 g, 20%), orange prisms, m.p. 93—94 °C (from light petroleum) (Found: C, 68.9; H, 6.9; N, 7.6. $C_{11}H_{13}NO_2$ requires C, 69.0; H, 6.8; N, 7.3%); $\nu_{max.}$(paste) 3 100 and 1 650 cm^{-1}; $\delta_H(CDCl_3)$ 1.20 (6 H, s), 2.75 (2 H, s), 6.95—7.2 (2 H, m), and 7.2—7.4 (2 H, m); $\delta_C(CDCl_3)$ 24.4 (CH_3), 37.6 (C), 39.5 (CH_2), 112.6 (CH), 122.3 (C), 123.6 (CH), 127.5 (CH), 127.8 (CH), 136.5 (C), and 170.2 (CO); *m/z* 191.0950 (M^+, 36%, $C_{11}H_{13}NO_2$ requires 191.0946), 175 ($C_{11}H_{13}NO$, 87), 160 ($C_{10}H_{10}NO$, 23), 148 ($C_9H_{10}NO$, 41), 147 (C_9H_9NO, 15), 146 ($C_{10}H_{12}N$, 33), and 132 ($C_9H_{10}N$, 100). This compound gave a purple colour with dilute ethanolic iron(III) chloride.

(ii) 3,3-*Dimethyl*-3,4-*dihydroquinolin*-2(1H)-*one* (**21i**) (0.4 g, 16%), m.p. 154 °C (from benzene–light petroleum) (Found: C, 75.4; H, 7.6; N, 7.9. $C_{11}H_{13}NO$ requires C, 75.4; H, 7.5; N, 8.0%); $\nu_{max.}$(paste) 3 200, 3 080, and 1 670 cm^{-1}; $\delta_H(CDCl_3)$ 1.20 (6 H, s), 2.77 (2 H, s), 6.8—7.05 (2 H, m), 7.1—7.3 (2 H, m), and 9.20 (1 H, br); $\delta_C(CDCl_3)$ 24.4 (CH_3), 37.2 (C), 40.2 (CH_2), 114.9 (CH), 122.7 (CH), 123.1 (C), 127.2 (CH), 128.2 (CH), 137.0 (C), and 177.2 (CO); *m/z* 175.0990 (M^+, 94%, $C_{11}H_{13}NO$ requires 175.0997), 160 ($C_{10}H_{10}NO$, 26), 147 (C_9H_9NO, 16), and 132 ($C_9H_{10}N$, 100).

Oxidation of Compound (**21a**) *with Hydrogen Peroxide and Sodium Tungstate*.—The amine (**21a**) was oxidised at 0 °C in aqueous methanol by hydrogen peroxide (30%) in the presence of sodium tungstate following the published procedure.[16] Preparative t.l.c. (silica gel, light petroleum–ether) isolated only the hydroxy amide (**21h**) (35%). None of the amide (**21i**) could be detected.

3,3-*Dimethylquinoline*-2,4(1H,3H)-*dione* (**21j**).—A mixture of the anilide (**23a**) (30 g), xylene (500 ml), and phosphorus pentaoxide (30 g) was boiled for 2 h. The solution was decanted from the insoluble material and evaporated to leave the *dione* (**21j**) (9.9 g, 35%), m.p. 195 °C (from benzene–light petroleum) (Found: C, 69.6; H, 6.0; N, 7.2. $C_{11}H_{11}NO_2$ requires C, 69.8; H, 5.9; N, 7.4%); $\nu_{max.}$(paste) 3 200, 3 120, 3 070, 1 700, and 1 670 cm^{-1}; $\delta_H(CDCl_3)$ 1.03 (6 H, s), 6.56 (1 H, d, *J* 8 Hz), 6.75 (1 H, t, *J* 8 Hz), 7.06 (1 H, t, *J* 8 Hz), 7.46 (1 H, d, *J* 8 Hz), and 9.47 (1 H, br); $\delta_C(CDCl_3)$ 23.5 (CH_3), 52.7 (C), 116.3 (CH), 118.4 (C), 123.5 (CH), 127.9 (CH), 135.9 (CH), 140.8 (C), 176.7 (CO), and 197.6 (CO), *m/z* 189 (M^+, 97%), 174 (34), 146 (14), and 119 (100).

Reduction of the Quinolin-2,4(1H,3H)-*dione* (**21j**).—The amide (**21j**) (2 g) was dissolved in a mixture of acetic acid (40 ml), acetic anhydride (1 g), and concentrated sulphuric acid (1 g) and the solution was hydrogenated (1 atm H_2) over a palladium catalyst (10% on charcoal) at room temperature for 12 h. The mixture was filtered, diluted with water (100 ml), and extracted with chloroform (2 × 100 ml). The chloroform extracts were washed with aqueous sodium hydrogencarbonate, dried, and evaporated, to leave the amide (**21i**) (1.3 g, 72%) identical with the product from peracid oxidation of (**21f**).

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References

1 Part 25, A. R. Evans and G. A. Taylor, *J. Chem. Soc., Perkin Trans. 1*, 1987, 567.
2 C. P. Falshaw, N. A. Hashi, and G. A. Taylor, *J. Chem. Soc., Perkin Trans. 1*, 1985, 1837.
3 R. Huisgen, H. Seidl, and I. Brüning, *Chem. Ber.*, 1968, **102**, 1102.
4 (*a*) M. A. Abou-Gharbia and M. M. Joullié, *J. Org. Chem.*, 1979, **44**, 2691; (*b*) A. R. Evans, M. Hafiz, and G. A. Taylor, *J. Chem. Soc., Perkin Trans. 1*, 1984, 1241.
5 R. N. Pratt and G. A. Taylor, *J. Chem. Soc. C*, 1967, 1569.
6 O. Exner and B. Kakáč, *Collect. Czech. Chem. Commun.*, 1960, **25**, 2530 (*Chem. Abstr.*, 1961, **55**, 3482).
7 R. N. Pratt and G. A. Taylor, *J. Chem. Soc. C*, 1968, 1653.
8 (*a*) R. N. Pratt, D. P. Stokes, and G. A. Taylor, *J. Chem. Soc., Perkin Trans. 1*, 1975, 498; (*b*) A. F. Gettins, D. P. Stokes, and G. A. Taylor, *ibid.*, 1977, 1849; (*c*) M. Hafiz and G. A. Taylor, *ibid.*, 1980, 1700.
9 A. R. Evans and G. A. Taylor, *J. Chem. Soc., Perkin Trans. 1*, 1983, 979.
10 H. Seidl, R. Huisgen, and R. Grashey, *Chem. Ber.*, 1969, **102**, 926.
11 Unpublished results.
12 (*a*) R. N. Pratt, D. P. Stokes, G. A. Taylor, and P. C. Brookes, *J. Chem. Soc. C*, 1968, 2086; (*b*) C. H. Hassall and A. E. Lippman, *J. Chem. Soc.*, 1953, 1059.
13 P. L. Southwick and L. L. Seivard, *J. Am. Chem. Soc.*, 1949, **71**, 2533.
14 G. R. Clemo and W. H. Perkin Jr., *J. Chem. Soc.*, 1924, **125**, 1608.
15 J. Thesing and H. Mayer, *Justus Liebigs Ann. Chem.*, 1957, **609**, 46.
16 M. Mitsui, S. Zenki, T. Shiota, and S. Murahashi, *J. Chem. Soc., Chem. Commun.*, 1984, 874.
17 J. R. Johnson and J. M. Witzel, *Org. React.*, 1946, **3**, 136.
18 W. Weyler Jr., W. G. Duncan, M. B. Liewen, and H. W. Moore, *Org. Synth.*, 1976, **55**, 32.
19 M. S. Newman and E. A. Zuech, *J. Org. Chem.*, 1962, **27**, 1436.
20 E. Schmitz, *Chem. Ber.*, 1958, **91**, 1488.
21 R. H. Hasek, R. D. Clark, E. U. Elam, and J. C. Martin, *J. Org. Chem.*, 1962, **27**, 60.
22 H. Staudinger and J. Meyer, *Helv. Chim. Acta*, 1919, **2**, 608.
23 W. H. Perkin, *J. Chem. Soc.*, 1903, **83**, 1246.

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