[2 + 2] Cycloadditions of Lithium Alkynamides Produced by Fragmentation of 5-Lithio-1-phenyl-1,2,3-triazoles

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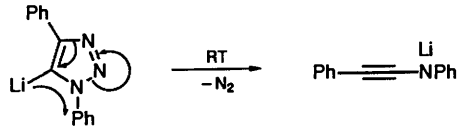
Three 1-phenyl-1,2,3-triazoles **1a–c** bearing substituents at the 4-position have been converted into the corresponding 5-lithio compounds. These undergo fragmentation and loss of nitrogen at room temperature. The *N*-phenylalkynamide salts **3** so produced have been intercepted in [2 + 2] cycloadditions. The salt derived from the triazole-4-carboxamide **1b** reacts with cyclohexanone and with 4-chlorobenzaldehyde by cycloaddition to the C=O bond; the cycloadducts then undergo ring-opening and the amides **5** and **7** are isolated. Analogous reactions are observed with the 4-(dihydroloxazol-2-yl)triazole **1c**: in this case the lithium salt also reacts with a Schiff base, 4-chloro-α-phenyliminotoluene, and with an electrophilic alkene, dimethyl fumarate. A cyclobutene diester, compound **12**, has been isolated from this last reaction. The lithium salt **3a** derived from 1,4-diphenyltriazole **1a** has similarly been intercepted by dimethyl fumarate and by nitrostyrenes. Structures **13** and **14** have been assigned to the products of these reactions.

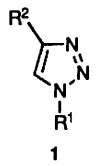
Several years ago Raap reported that 1,4-diphenyl-1,2,3-triazole **1a** underwent hydrogen–lithium exchange at C-5 and that the resulting triazolyl-lithium species was unstable above room temperature.[1] The ring system undergoes fragmentation as shown in Scheme 1; the acyclic lithium salt so formed was



Scheme 1

intercepted by acylation. Schöllkopf and Hoppe subsequently showed that this acyclic intermediate could be intercepted by carbonyl compounds to give oxetanes: thus, cyclohexanone gave the oxetane **2** in good yield.[2] This triazole fragmentation is one of a group of similar reactions which take place with carbanions derived from five-membered heteroaromatic compounds.[3] The reactions would be a useful way of producing a variety of four-membered rings if the [2 + 2] cycloaddition process could be extended to other lithium intermediates and to reaction partners other than ketones. An analogous fragmentation of an isoxazol-5-yl-lithium species has already been used as a method of synthesis of β-lactams.[4]

We set out to explore variants of the cycloaddition based on the fragmentation of 5-lithio-1,2,3-triazoles. We have investigated the reactions of triazoles with substituents other than phenyl at C-1 or C-4. The 5-lithio derivatives of three triazoles, compound **1a**, the diethylamide **1b**, and the dihydrooxazolyltriazole **1c**, have been generated and then warmed to induce the loss of nitrogen. Cycloadditions of the resulting lithium alkynamides have been attempted with carbonyl compounds, imines, and electron deficient alkenes. The structures of the products isolated from several of these reactions are consistent with an initial [2 + 2] cycloaddition having taken place. Three other 1,2,3-triazoles have been prepared, namely 1-benzyl-4-phenyl-1,2,3-triazole **1d**, 4-phenyl-1-(α-styryl)-1,2,3-triazole **1e**, and 4-nitro-1-phenyl-1,2,3-triazole **1f**. We have also attempted to generate the 5-lithio derivatives of these three triazoles, but no products derived from fragmentation reactions have been isolated.



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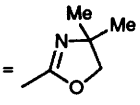
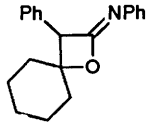
1a; $R^1 = R^2 = Ph$
b; $R^1 = Ph$; $R^2 = CONEt_2$
c; $R^1 = Ph$; R^2 =



d; $R^1 = CH_2Ph$, $R^2 = Ph$
e; $R^1 = C(Ph) = CH_2$, $R^2 = Ph$
f; $R^1 = Ph$, $R^2 = NO_2$



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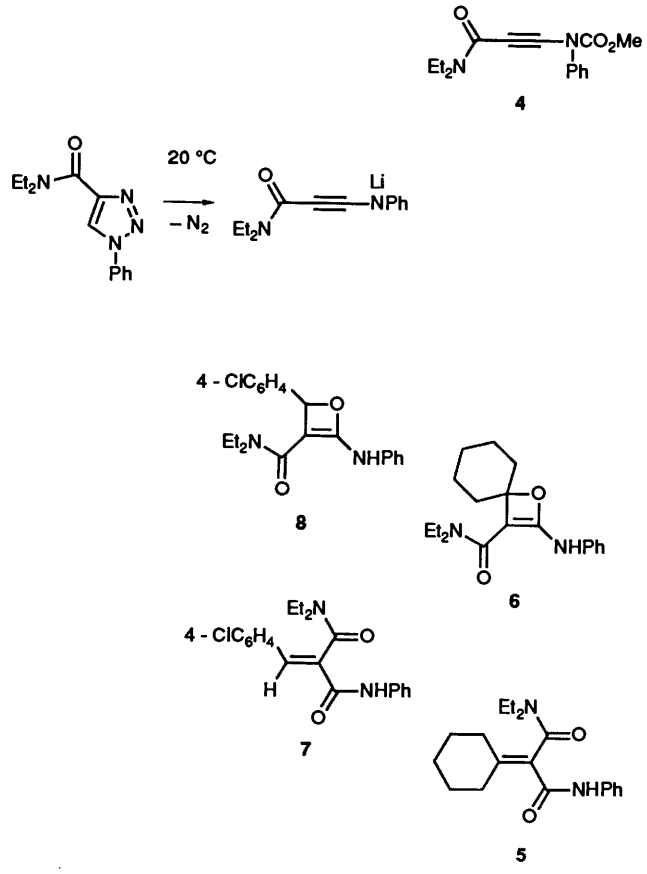
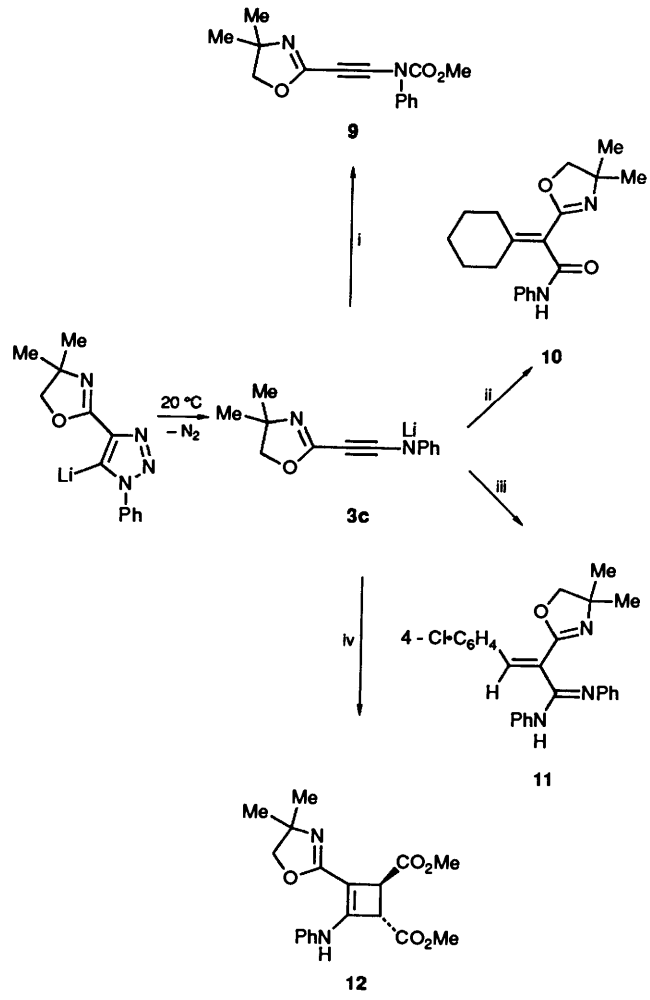
All the triazoles except compounds **1b** and **1c** have been reported previously. The known compounds were prepared by the literature methods, which require cycloaddition of the appropriate azides to phenylacetylene (for **1a**,[5] **1d**[5] and **1e**[6]) or to 2-(4-morpholino)-1-nitroethylene (for **1f**[7]). 1-Phenyl-1,2,3-triazole-4-carboxylic acid was prepared from azidobenzene and the sodium salt of ethyl 3-oxopropanoate by a literature procedure.[8] This acid was then converted into the derivatives **1b** and **1c** by standard methods.

The triazoles **1b** and **1c** were selected for investigation for two reasons. First, as carboxylic acid derivatives, any cycloadducts derived from them should be capable of useful functional group transformations. Second, the functional groups are known to be efficient *ortho*-directing groups for *C*-lithiation[9] and it was therefore expected that they could be lithiated efficiently. The latter expectation was fulfilled for **1c** but not for **1b** since neither butyllithium nor *sec*-butyllithium proved to be suitable for lithiation of the triazole at C-5. After some experimentation it was found that **1b** could be cleanly lithiated by using lithium diisopropylamide (LDA) in excess at −78 °C. The diphenyltriazole **1a** was lithiated using butyllithium, as reported previously.[1] Fragmentation of the triazol-5-yllithium species derived from **1a**, **1b** and **1c** took place at room temperature. After the triazoles had been converted into their 5-lithio derivatives **3** at −78 °C the solutions were allowed to warm to room temperature and nitrogen was evolved. The solutions were then cooled to −78 °C and electrophiles were added.

Products which were isolated from the reactions of the species



Scheme 2 *Reagents:* i, MeOCOCl; ii, cyclohexanone; iii, 4-Cl-C_6H_4CHO



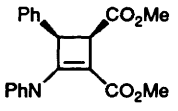
Scheme 3 *Reagents:* i, MeOCOCl; ii, cyclohexanone; iii, 4-Cl-$C_6H_4CH{=}NPh$; iv, (*E*)-$MeO_2CCH{=}CHCO_2Me$

3b are shown in Scheme 2. Methyl chloroformate gave the alkynylamide **4**, by an acylation which is analogous to that reported by Raap for **3a**.[1] Cyclohexanone gave the unsaturated amide **5** which was derived from an isolable but unstable precursor: this precursor is tentatively assigned the oxetene structure **6** on the basis of its IR spectrum and by analogy with reactions reported for **3a**.[2] 4-Chlorobenzaldehyde similarly gave the diamide **7** as a single isomer: it is assigned the structure shown on the basis of the preferred direction of ring opening of a precursor oxetene **8**. The oxetene was not detected in this case. (A similar stereoselective ring-opening of an oxetene derived from the Lewis acid catalysed addition of an aldehyde to a silyloxyacetylene has recently been postulated[10]). Several other electrophiles were added to solutions of **3b** but there was no evidence that they reacted with it. These included carbon disulphide, 4-chloro-α-phenyliminotoluene and 3,4-dihydroisoquinoline: evidently, the imines were not sufficiently electrophilic to intercept the anion.

The species **3c** proved to be slightly more reactive and a wider range of additions was attempted with it (Scheme 3). Methyl chloroformate and cyclohexanone gave products **9** and **10** analogous to those obtained from **3b**. An adduct, which was assigned the structure **11**, was also obtained from 4-chloro-α-phenyliminotoluene. This compound is presumably formed by [2 + 2] addition followed by rearrangement but no intermediate cycloadduct could be detected. We attempted to use the addition to the C=N bond as a means of ring expansion of a cyclic imine, 3,4-dihydroisoquinoline. Unfortunately, this imine failed to react, even when the reaction mixture was heated. Reaction of **3c** with dimethyl fumarate gave a crystalline 1:1 adduct which was isolated in moderate yield. The ^1H and ^{13}C NMR spectra of this compound were consistent with the cyclobutene structure **12**. In particular, both methoxycarbonyl groups are attached to sp^3 carbon and the coupling constant of 1.5 Hz is consistent with a *trans* relationship of the ring hydrogen atoms. A reaction was also attempted with methyl vinyl ketone. This gave an unstable product in low yield. The presence of signals for vinylic hydrogen atoms in the NMR spectrum (δ 5.4–5.7) was consistent with addition having occurred at the C=O bond rather than at the C=C bond; however, we were unable to characterise the product.

The successful addition of dimethyl fumarate to **3c** led us to attempt a similar addition to the diphenyl species **3a**. This reaction gave a crystalline product in moderate yield (42%) after chromatography. The presence of an NH group and two types of carbonyl group (ν_{max}/cm^{-1} 1745 and 1665) was indicated by the IR spectrum. The ^{13}C and ^1H NMR spectra were in accord with cyclobutene structure for the product. The data are consistent with its formulation as the cyclobutene diester **13**, which could be formed by [2 + 2] cycloaddition followed by proton shifts. Such a process would be expected to give the thermodynamically most stable isomer. We had assumed that this would be the structure in which the phenyl and methoxycarbonyl groups are *trans*. However the H–H coupling constant (5.0 Hz) is higher than normally observed for a *trans*-disubstituted cyclobutene.[11] The value is more consistent with structure **13** in which the phenyl and methoxycarbonyl groups are *cis*, and we have therefore tentatively assigned this stereochemistry to it. Compound **3a** also reacted with nitroalkenes. β-Nitrostyrene gave a yellow crystalline product (48%) for which the spectroscopic data are consistent with

structure **14a**: again the H–H coupling constant (5.4 Hz) is better accommodated by a *cis* arrangement. 4-Chloro-β-nitrostyrene gave an analogous product **14b**. The adducts formed in these reactions can be compared with those described by Pennings and Reinhoudt from the addition of β-nitrostyrene to the ynamine 1-phenyl-2-pyrrolidin-1-ylacetylene.[12] Two 1:1 adducts were isolated to which the structures **15** and **16** were assigned. The spectra recorded for **14a** rule out structures analogous to either of these. In the case of **14a** the presence of a hydrogen substituent on the amine nitrogen may permit hydrogen bonding to the nitro group in the nitroenamine structure.



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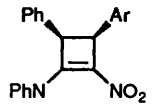
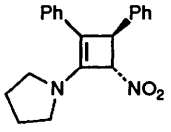


14 **a**; Ar = Ph
b; Ar = C_6H_4Cl-4



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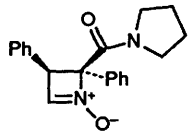

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Attempts to carry out analogous reactions with the triazoles **1d**, **1e** and **1f** were all unsuccessful, but for differing reasons. The 1-benzyltriazole **1d** was successfully *C*-lithiated with butyllithium but the ring system remained intact when the solution was warmed to room temperature or above. Clearly, the nature of the 1-substituent influences the propensity to fragmentation. Reaction with methyl chloroformate at room temperature gave the methyl 1,2,3-triazole-5-carboxylate **17** as the major product. The corresponding 1-styryltriazole **1e** was also lithiated with butyllithium, and nitrogen was evolved when the soluton was warmed. However, reaction of the product with methyl chloroformate gave a mixture in which the major component appeared to result from electrophilic attack on the terminus of the carbon–carbon double bond of the styryl group (by NMR). The product was not characterised and these reactions were not pursued. With the 4-nitrotriazole **1f** we were unable to find conditions which permitted lithiation at C-5 without attack at the nitro group.

We have thus shown that the triazole fragmentation discovered by Raap is capable of extension to triazoles with functional groups at C-4. The trapping of the intermediate alkynylamide anions by electrophiles has been extended, although the results are variable and unpredictable. Electrophilic alkenes appear to be the most promising of the new reagents which have been used since they give cyclobutenes in moderate yield. There are unexpected problems in assigning stereochemistry to some of these cycloadducts which we intend to resolve by further work. The results with imines as electrophiles were mostly unproductive, but there is scope for further investigation of such reactions using more activated imines and other electrophilic π-bonded compounds which have already been shown to undergo cycloaddition to ynamines.[13]

Experimental

^{1}H NMR spectra were recorded at 250 MHz on a Bruker WM250 instrument, and at 220 MHz using a Perkin-Elmer R34 instrument, in deuteriochloroform (except where indicated otherwise) and with tetramethylsilane as an internal reference. Signals are singlets unless indicated otherwise. *J* Values are given in Hz. ^{13}C NMR spectra were recorded at 62.9 MHz. Mass spectra were recorded under electron impact on a VG Micromass 7070E instrument. Microanalyses were performed in the microanalytical laboratory at Liverpool University. Melting points were obtained on a Reichert hot stage apparatus and are uncorrected. THF (tetrahydrofuran) and diethyl ether were distilled from sodium–benzophenone ketyl immediately before use. Flash column chromatography[14] was carried out using Merck 9385 silica gel.

1,4-*Diphenyl*-1,2,3-*triazole* **1a**[5].—This was prepared (42%) by the procedure described[5] from azidobenzene (11.9 g, 0.1 mol) and phenylacetylene (20.4 g, 0.2 mol) in toluene (100 cm^3). It had m.p. 180–183 °C (from toluene) (lit.,[5] 184–185 °C).

N,N-*Diethyl*-1-*phenyl*-1,2,3-*triazole*-4-*carboxamide* **1b**.—1-Phenyl-1,2,3-triazole-4-carboxylic acid was prepared (31%) by the procedure described by Huisgen *et al.*[8] from azidobenzene (7.31 g, 61.4 mmol) and the sodium salt of ethyl 3-oxopropanoate[15] (6.60 g, 47.8 mmol) in ethanol (100 cm^3). It had m.p. 141–142 °C (lit.,[8] 142–143 °C); δ(CF_3CO_2H) 7.66 (3 H, m), 7.78 (2 H, d) and 8.92 (1 H, 5-H). The acid (2.78 g, 14.7 mmol) was converted into its chloride by heating with thionyl chloride (20 cm^3) under reflux for 3 h. The crude acid chloride was heated with diethylamine (3.0 cm^3) in dichloromethane for 2 h. The solvent was distilled off and the solid residue was crystallised to give the *carboxamide* **1b** (3.32 g, 92%), m.p. 121–122 °C (from tetrachloromethane) (Found: C, 63.9; H, 6.6; N, 23.0. $C_{13}H_{16}N_4O$ requires C, 63.9; H, 6.6; N, 22.9%); ν_{max}(KBr)/cm^{-1} 1613 (C=O); δ_H(250 MHz) 1.26 (3 H, t), 1.36 (3 H, t), 3.58 (2 H, q), 4.04 (2 H, q), 7.50 (3 H, m), 7.76 (2 H, d) and 8.56 (1 H); *m/z* 244 (M^+), 173 and 144.

4-(4,5-*Dihydro*-4,4-*dimethyloxazol*-2-*yl*)-1-*phenyl*-1,2,3-*triazole* **1c**.—1-Phenyl-1,2,3-triazole-4-carbonyl chloride was prepared as described for triazole **1b**. The acid chloride (6.1 g, 29.4 mmol) in dichloromethane (30 cm^3) was added dropwise to a stirred solution of 2-amino-2-methylpropan-1-ol (5.24 g, 58.8 mmol) in dichloromethane (14 cm^3) at 0 °C. The reaction mixture was stirred overnight at room temperature and the solvent was then distilled off. The residue was acidified with 2 mol dm^{-3} hydrochloric acid and extracted with ethyl acetate (3 × 25 cm^3). The extracts were washed with brine, dried ($MgSO_4$), and evaporated to give a beige solid, which was identified from its spectra as *N*-(1-hydroxy-2-methylpropan-2-yl)-1-phenyl-1,2,3-triazole-4-carboxamide (7.53 g, 98%); ν_{max}(Nujol)/cm^{-1} 3380, 3340 and 1655; δ_H(220 MHz) 1.51 (6 H), 2.08 (1 H, br), 3.82 (2 H), 7.49 (3 H, m), 7.74 (2 H, d) and 8.68 (1 H).

Thionyl chloride (11.2 g, 94 mmol) was added dropwise with stirring to this amide (7.50 g, 29 mmol). After the initially vigorous reaction had subsided the solution was stirred for 1 h, the excess of thionyl chloride was distilled off, and the residue was made alkaline with aq. sodium hydroxide. Extraction with ethyl acetate (3 × 25 cm^3) gave the crude triazole (6.06 g, 87%), m.p. 103–105 °C. Recrystallisation gave the *triazole* **1c**, m.p. 105–107 °C (from tetrachloromethane) (Found: C, 64.3; H, 5.9; N, 23.3. $C_{14}H_{14}N_4O$ requires C, 64.4; H, 5.8; N, 23.1%); ν_{max}(KBr)/cm^{-1} 1679 (C=O); δ_H[250 MHz; $(CD_3)_2CO$] 1.32 (6 H), 4.12 (2 H), 7.55 (3 H, m), 7.98 (2 H, m) and 8.88 (1 H); *m/z* 242 (M^+).

2-*Benzyl*-4-*phenyl*-1,2,3-*triazole* **1d**[5].—Benzyl azide (10.0 g, 0.075 mol) and phenylacetylene (15.3 g, 0.15 mol) in toluene (75 cm^3) gave the triazole **1d** (5.0 g, 28%), m.p. 127–128 °C (lit.,[5] 128–128.5 °C).

4-Phenyl-1-(1-phenylvinyl)-1,2,3-triazole **1e**[6].—This triazole was prepared (48%) as described previously[6] from phenylacetaldehyde (5.6 g, 46.6 mmol), α-azidostyrene (7.0 g, 48.2 mmol) and potassium *tert*-butoxide.

4-Nitro-1-phenyl-1,2,3-triazole **1f**[7].—4-(2-Nitrovinyl)-morpholine[16] (4.76 g, 30 mmol) and azidobenzene (7.17 g, 60 mmol) were mixed and the mixture was divided among five Carius tubes. These were sealed and heated at 100 °C for 10 h. They were cooled and carefully opened (with the release of a considerable volume of gas). The black residue was dissolved in chloroform and the solution was filtered through alumina. The solvent was distilled off and the residue was triturated with light petroleum (b.p. 60–80 °C) to give the triazole **1e** (3.17 g, 55%), m.p. 132–133 °C (lit.,[7] 134 °C).

Lithiation and Fragmentation of the Triazole **1b**.—*General procedure.* LDA was formed by the reaction of diisopropylamine (4 cm^3) with butyllithium (2.66 mmol) in hexane under nitrogen at room temperature. After 10 min the solvent was removed to leave a solid which was dissolved in THF (10 cm^3). The solution was cooled to −78 °C and a solution of the triazole **1b** (0.30 g, 1.23 mmol) in THF (5 cm^3) was added. The solution was kept cold for 15 min and then allowed to warm to room temperature. Gas was evolved steadily at room temperature; evolution of gas ceased after 1 h. The solution containing the species **3b** was cooled to −78 °C and a solution of the electrophile in THF was added dropwise. The reaction mixture was stirred for 10 min and then allowed to warm to room temperature. The solvent was evaporated off and the residue was partitioned between ether and water. The ethereal solution was dried and evaporated to leave the crude product which was purified by flash chromatography. The following were prepared by this method.

N,N-Diethyl-3-(N-methoxycarbonylanilino)propynamide **4**. Methyl chloroformate (0.21 cm^3, 2.66 mmol) was added to the solution of **3b**. Flash chromatography (ether–dichloromethane 1:9) gave the *amide* **4** (0.25 g, 74%) as a yellow oil [Found: C, 65.2; H, 6.9; N, 10.9%; *m/z* 274.1314 (M^+). $C_{15}H_{18}N_2O_3$ requires C, 65.7; H, 6.6; N, 10.2%; *m/z* 274.1317]; ν_{max}(film)/cm^{-1} 2220, 1750 and 1625; δ_H(250 MHz) 1.12 (3 H, t), 1.19 (3 H, t), 3.42 (2 H, q), 3.52 (2 H, q), 3.86 (3 H) and 7.26–7.44 (5 H, m).

N,N-Diethyl-N′-phenylcyclohexylidenemalonamide **5**. Cyclohexanone (0.123 g, 1.23 mmol) gave, after flash chromatography (ether), a pale yellow oil (0.24 g, 62%), which on the basis of its IR spectrum, was tentatively assigned structure **6**: ν_{max}(film)/cm^{-1} 1730 and 1630. When allowed to stand for a short time this gave colourless crystals of the *diamide* **5**, m.p. 120–122 °C (from hexane) [Found: C, 72.7; H, 8.5; N, 8.9%; *m/z* 314.1944 (M^+). $C_{19}H_{26}N_2O_2$ requires C, 72.6; H, 8.3; N, 8.9%; *m/z* 314.1994]; ν_{max}(KBr)/cm^{-1} 1660 and 1590; δ_H(250 MHz) 1.14 (3 H, t), 1.17 (3 H, t), 1.62 (6 H, br), 2.15 (2 H, br), 2.57 (2 H, br), 3.47 (4 H, q), 7.07 (1 H, m), 7.29 (2 H, m), 7.56 (2 H, m) and 8.57 (1 H, NH).

N,N-Diethyl-N′-phenyl-4-chlorobenzylidenemalonamide **7**. 4-Chlorobenzaldehyde (0.17 g, 1.23 mmol) gave a gum (0.43 g) which by flash chromatography (ether–hexane 3:2) gave the *diamide* **7** (0.16 g, 36%), m.p. 105–107 °C (from hexane–tetrachloromethane) (Found: C, 67.1; H, 5.85; N, 7.7. $C_{20}H_{21}ClN_2O_2$ requires C, 67.3; H, 5.9; N, 7.85%); ν_{max}(KBr)/cm^{-1} 3260, 3230, 1660 and 1595; δ_H(250 MHz) 0.83 (3 H, t), 1.18 (3 H, t), 3.26 (2 H), 3.75 (2 H), 7.10 (1 H, m), 7.33 (6 H, m), 7.58 (2 H, d), 7.61 (1 H) and 8.83 (1 H, NH); δ_C(^{13}C) 12.08 (q), 13.88 (q), 39.71 (t), 43.24 (t), 120.21 (d), 124.61 (d), 129.05 (d), 130.47 (d), 131.46 (s), 132.25 (s), 135.95 (d), 137.73 (s), 162.02 (s) and 168.44 (s); *m/z* 358, 356 (M^+) and 266, 264 ($M^+ - Et_2N$).

Lithiation and Fragmentation of the Triazole **1c**.—*General procedure.* A solution of the triazole **1c** (0.50 g, 2.06 mmol) in THF (8 cm^3) was added dropwise to a stirred solution of butyllithium (2.27 mmol) in THF (5 cm^3) at −78 °C under N_2. A colourless precipitate formed. After 15 min the cooling bath was removed and the reaction mixture was allowed to warm to room temperature. Gas evolution was rapid at room temperature and ceased after 1 h. The red–brown solution was cooled to −78 °C and a solution of the electrophile (2.06 mmol) in THF (5 cm^3) (or an excess as stated) was added. After 10 min the mixture was allowed to warm to room temperature. The solvent was distilled off and the residue was extracted with dichloromethane (75 cm^3). The solution was washed with water, dried and evaporated.

The following were isolated using this procedure:

1-(4,5-Dihydro-4,4-dimethyloxazol-2-yl)-2-(N-methoxycarbonylanilino)ethyne **9**. Methyl chloroformate (1 cm^3) gave a gum (0.50 g) from which was isolated by flash chromatography (ether) the oxazoline **9** (0.17 g, 30%) as an oil; ν_{max}(film)/cm^{-1} 2250 and 1745; δ_H 1.29 (6 H), 3.89 (3 H), 3.94 (2 H) and 7.26–7.46 (5 H, m). The compound was not characterised further.

2-Cyclohexylidene-2-(4,5-dihydro-4,4-dimethyloxazol-2-yl)-N-phenylacetamide **10**. Cyclohexanone (0.24 cm^3, 2.27 mmol) gave the *amide* **10** (0.63 g, 98%), m.p. 173–175 °C (from ether–tetrachloromethane) (Found: C, 73.2; H, 7.8; N, 9.0 $C_{19}H_{24}N_2O_2$ requires C, 73.05; H, 7.7; N, 9.0%); ν_{max}(KBr)/cm^{-1} 3270, 1650, 1625 and 1600; δ_H 1.34 (6 H), 1.72 (6 H, br), 2.40 (2 H, t), 2.70 (2 H, t), 4.01 (2 H), 7.05 (1 H, t), 7.28 (2 H, t), 7.57 (2 H, d) and 9.03 (1 H, NH); *m/z* 312 (M^+), 220 and 193.

3-(4-Chlorophenyl)-2-(4,5-dihydro-4,4-dimethyloxazol-2-yl)-N,N′-diphenylpropenamidine **11**. 4-Chloro-α-phenyliminotoluene (0.49 g, 2.27 mmol) gave, after flash chromatography (ether–hexane, 7:3), unchanged imide (0.20 g) and the *amidine* **11** (0.55 g, 95% based on imide consumed), m.p. 121–123 °C (from tetrachloromethane–hexane) (Found: C, 72.6; H, 5.65; N, 9.7. $C_{26}H_{24}ClN_3O$ requires C, 72.6; H, 5.6; N, 9.8%); ν_{max}(KBr)/cm^{-1} 1642 and 1623; δ_H(250 MHz) 1.19 (6 H), 3.85 (2 H) and 6.96–7.53 (16 H, m); *m/z* 431 and 429 (M^+).

Dimethyl 2-(4,5-dihydro-4,4-dimethoxyloxazol-2-yl)-1-anilinocyclobutene-3,4-dicarboxylate **12**. Dimethyl fumarate (0.30 g, 2.06 mmol) gave, after flash chromatography and trituration of the major fraction with ether, the *cyclobutene diester* **12** (0.25 g, 34%), m.p. 114–116 °C (from tetrachloromethane) (Found: C, 63.9; H, 6.2; N, 7.7. $C_{19}H_{22}N_2O_5$ requires C, 63.7; H, 6.2; N, 7.8%); ν_{max}(KBr)/cm^{-1} 3208, 1742, 1691 and 1658; δ_H(250 MHz) 1.02 (3 H), 1.06 (3 H), 3.69 (1 H, d, *J* 1.50), 3.70 (1 H, d, *J* 1.50), 3.73 (3 H), 3.77 (3 H), 4.27 (1 H), 4.28 (1 H), 6.98–7.06 (3 H, m), 7.27 (2 H, t) and 7.75 (1 H, br, NH); δ_C(^{13}C) 27.76 (q), 43.84 (d), 44.52 (d), 50.80 (q), 52.28 (q), 67.34 (s), 79.33 (t), 97.48 (s, cyclobutene *C*-oxazolinyl), 118.51 (d, Ar), 123.67 (d, Ar), 129.45 (d, Ar), 138.33 (s, Ar), 151.36 (s, cyclobutene *C*-NHPh), 161.15 (s) and 163.46 (s); *m/z* 358 (M^+), 299 and 267.

Reaction of **3c** *with But-3-en-2-one.*—The freshly distilled ketone (0.17 cm^3, 2.1 mmol) was added to a solution of the salt **3c** (2.06 mmol) at −78 °C. Flash chromatography (ether) gave a yellow solid (0.12 g); ν_{max}(Nujol)/cm^{-1} 3250, 1650 and 1600; δ_H 1.30, 4.00, 5.4–5.6 (m) and 7.1–7.6 (m). The solid decomposed rapidly and it was not characterised further.

Adducts from **3a**.—*(a) Dimethyl 2-anilino-3-phenylcyclobutene-1,4-dicarboxylate* **13**. Dimethyl fumarate (0.33 g, 2.26 mmol) and **3a** (2.26 mmol) gave a yellow gum (0.86 g) from which was isolated by flash chromatography (ether–light petroleum 3:2) the *cyclobutene diester* **13** (0.32 g, 42%) as colourless crystals, m.p. 123–126 °C (from ether) (Found: C, 71.3; H, 5.7; N, 4.2. $C_{20}H_{19}NO_4$ requires C, 71.2; H, 5.7; N, 4.15%); ν_{max}(KBr)/cm^{-1} 3337, 1745 and 1665; δ_H 3.13 (3 H), 3.77

(3 H), 4.11 (1 H, d, *J* 5.0), 4.83 (1 H, d, *J* 5.0), 6.80–6.90 (3 H, m), 7.05–7.15 (2 H, m) and 7.18 (5 H); $\delta_C(^{13}C)$ 47.72 (q), 50.77 (d), 51.16 (d), 51.25 (q), 96.93 (s), 117.21 (d), 122.76 (d), 127.66 (d), 127.99 (d), 128.24 (d), 129.25 (d), 134.60 (s), 138.64 (s), 153.49 (s), 164.23 (s) and 171.16 (s); *m/z* 337 (M^+), 246 and 162.

(*b*) 2-*Anilino*-1-*nitro*-3,4-*diphenylcyclobutene* **14a**. 1-Nitro-2-phenylethene (0.34 g, 2.26 mmol) and **3a** (2.26 mmol) gave, by trituration of the crude reaction product and crystallisation, the nitrocyclobutene **14a** (0.37 g, 48%) as a yellow solid, m.p. 152–155 °C (from tetrachloromethane) [Found: C, 76.5; H, 5.2; N, 8.1%; *m/z* 342.1368 (M^+). $C_{22}H_{18}N_2O_2$ requires C, 77.2; H, 5.2; N, 8.1%; *m/z* 342.1368]; ν_{max}(KBr)/cm^{-1} 3282, 3259, 1649, 1599 and 1356; δ_H(250 MHz) 4.84 (1 H, d, *J* 5.4), 5.01 (1 H, d, *J* 5.4), 6.88–7.23 (15 H, m) and 9.38 (1 H, NH); $\delta_C(^{13}C)$ 51.57 (d), 51.64 (d), 118.66–129.59 (unresolved signals), 133.04 (s), 135.53 (s), 137.03 (s) and 151.13 (s).

(*c*) 2-*Anilino*-4-(4-*chlorophenyl*)-1-*nitro*-3-*phenylcyclobutene* **14b**. 2-(4-Chlorophenyl)-1-nitroethene[17] (0.36 g, 1.94 mmol) and **3a** (1.94 mmol) gave, by flash chromatography, the nitrocyclobutene **15b** (0.17 g, 23%) as yellow crystals, m.p. 153–155 °C (from tetrachloromethane) [Found: *m/z* 376.0979 (M^+). $C_{22}H_{17}{}^{35}ClN_2O_2$ requires *m/z* 376.0978]; δ_H(250 MHz) 4.86 (1 H, d, *J* 5.1), 4.97 (1 H, d, *J* 5.1), 6.84–7.26 (14 H, m) and 9.39 (1 H, NH).

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