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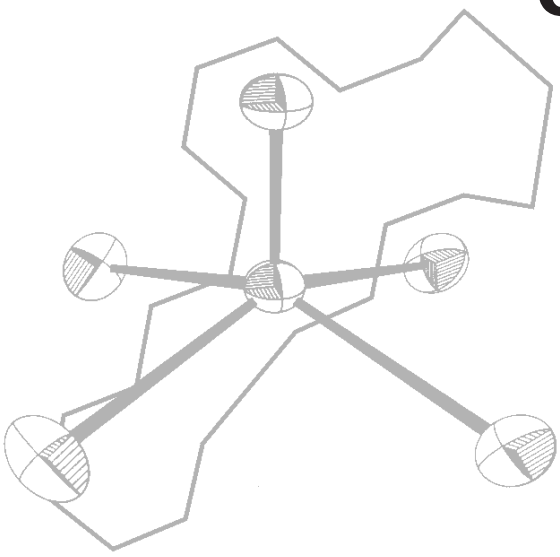

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The Reaction of 1,2-Diones with Ureas— a Synthesis of 4-(1-Substituted)alkylimidazol-2-ones

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The reaction between glyoxal and ureas or thioureas in formic acid in the presence of sulfinates gives 4-arylsulfonylimidazol-2-ones such as (3b) and (3e). Labile 4-arylsulfonyl-5-hydroxyimidazolidin-2-ones (2a–c) may be isolated. Acyclic or cyclic 1,2-diketones react with ureas in the presence of selected nucleophiles to give side-chain substituted imidazol-2-ones (5a–e).

Keywords. Synthesis; ureas; thioureas; imidazolones; diones; glyoxal.

The reaction between 1,2-dicarbonyl compounds and simple ureas can provide[1] an array of condensation products. In the simplest example, glyoxal is known[2] to react with urea to provide 4,5-dihydroxyimidazolidin-2-one (1a), isolable in good yield.

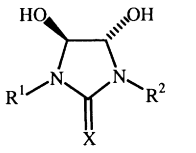
It seemed likely that reactive intermediates of this kind might incorporate suitably chosen nucleophiles to afford an assortment of novel products suitable for biological testing. Indeed, it has recently been shown[3] that (1a) may be reacted with an arylsulfinic acid to form a labile 4-arylsulfonyl-5-hydroxyimidazolidin-2-one (2a) which readily dehydrates to the 4-arylsulfonyl-1,3-dihydroimidazol-2-one (3a).

When t-butylurea was warmed with a solution of aqueous glyoxal and formic acid in the presence of sodium *p*-toluenesulfinate for 25 min the imidazolone (3b) was obtained in 82% yield as a single regioisomer. The same components at room temperature for 7 h in aqueous acetic acid gave the precursor (2b) analogous to the findings of Shutalev and Sivova.[3]

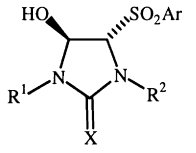
Surprisingly, a solution of (2b) in a mixture of (D_6)-dimethyl sulfoxide and (D)chloroform showed peaks attributable only to (3b). Despite its origins in dilute acetic acid, the trace of mineral acid normally present in (D)chloroform was sufficient to cause a very rapid and efficient transformation into the imidazolone (3b). This synthesis generated only one of the two possible imidazolone products, (3b), with selectivity seemingly arising from a requirement to minimize interactions between the two bulky groups. However, ethylurea, a somewhat less sterically demanding precursor, likewise gave a single isomer (3c). N.O.e. experiments carried out on (3c) indicated interactions between the alkene proton and the methylene of the ethyl group providing verification of the assumed 1,3-disubstitution pattern.

It was further found that 4-ethoxyphenylurea reacted with glyoxal in warm formic acid to give a mixture of isomers, presumably (3d) and its regioisomer, in a ratio of approximately 3 : 2. However, regioselectivity was observed from the same reaction components when they were reacted over 24 h in 30% aqueous acetic acid at room temperature to afford the intermediate imidazolidinone (2d) as a single isomer. A solution of this compound in (D)chloroform for 24 h at room temperature was converted quantitatively into a single imidazolone isomer (3d).

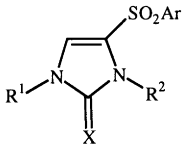
It seemed likely that condensations of this type should also provide a useful route to imidazolo-2-thiones. Indeed, reaction was found to occur readily between 1,3-dimethyl-



	X	R^1	R^2
(1a)	O	H	H
(1b)	O	Bu^t	H
(1c)	O	Et	H
(1d)	O	4-$EtOC_6H_4$	H
(1e)	S	Me	Me



	X	R^1	R^2	Ar
(2a)	O	H	H	Ph
(2b)	O	Bu^t	H	4-MeC_6H_4
(2c)	O	Et	H	4-MeC_6H_4
(2d)	O	4-$EtOC_6H_4$	H	Ph
(2e)	S	Me	Me	4-MeC_6H_4



	X	R^1	R^2	Ar
(3a)	O	H	H	Ph
(3b)	O	Bu^t	H	4-MeC_6H_4
(3c)	O	Et	H	4-MeC_6H_4
(3d)	O	4-$EtOC_6H_4$	H	Ph
(3e)	S	Me	Me	4-MeC_6H_4

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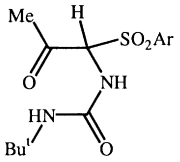
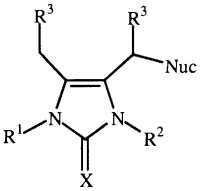
thiourea and glyoxal in aqueous acetic acid containing sodium *p*-toluenesulfinate to afford the anticipated imidazolo-2-thione (3e) in 70% yield.

It was of additional interest to evaluate the opportunities for extending the scope of this reaction. Hence pyruvaldehyde, the simplest monoketo candidate, was also examined. A mixture of t-butylurea, pyruvaldehyde and sodium *p*-toluenesulfinate in aqueous acetic acid gave an acyclic product (4) in which only the formyl group had reacted. By contrast, under these conditions glyoxal gave the cyclic 5-hydroxyimidazolidinone (2b). Attempts to cyclize (4) under mildly acidic conditions resulted in extensive decomposition.



(4)

Urea reacted, albeit slowly, with hexane-3,4-dione in formic acid containing sodium *p*-toluenesulfinate to form one major product. Surprisingly, one of the ethyl groups of the diketone was transformed into a 1-substituted ethyl group, bearing the toluenesulfonyl group as a substituent as in (5a). A proposed sequence of events for the formation of products of this kind is displayed in Scheme 1.



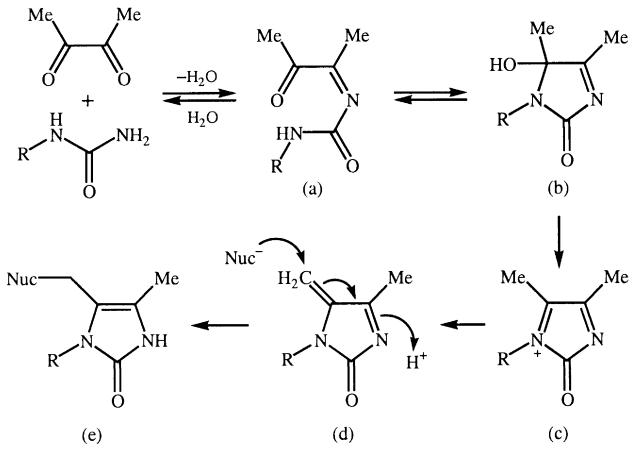
	X	R^1	R^2	R^3	Nuc
(5a)	O	H	H	Me	Ts
(5b)	O	Me	Me	H	Ts
(5c)	S	H	H	H	Ts
(5d)	O	H	H	Me	$SCH(Me)CO_2H$
(5e)	O	H	Bu	H	benzotriazol-1-yl
(5f)	O	4-$EtOC_6H_4$	H	H	Ts

Ts = toluenesulfonyl

Likewise, 1,3-dimethylurea reacted with diacetyl (butane-2,3-dione) in the presence of sodium *p*-toluenesulfinate, forming (5b), while thiourea gave (5c).

To summarize, it is evident that alternate pathways can prevail during an apparently simple condensation occurring between a urea and a 1,2-dicarbonyl compound in the presence of a suitable nucleophile.

Thus, where the dicarbonyl compound consists of two aldehyde groups (glyoxal), the initial product is a cyclic imidazolidinone (2) which easily dehydrates and the nucleophile is found attached directly to the resultant imidazolone ring (3). With a monoaldehyde/monoketone combination such as pyruvaldehyde the outcome is an acyclic condensation product (4).



Scheme 1

With a dialkyl 1,2-diketone, on the other hand, an imidazol-2-one (5) is again formed but the nucleophile becomes attached at the 1-position of one of the alkyl groups during an anomalous substitution reaction (Scheme 1).

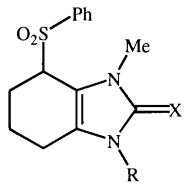
It was evident that the variety of products of type (5) might easily be increased by using alternative nucleophiles. Thus it was found that the thiol 2-mercaptopropionic acid also reacted readily with a mixture of urea and hexane-3,4-dione to give the expected product (5d).

Benzotriazole has also received wide application as a versatile nucleophile[4] under acidic conditions and it also formed the benzotriazole-substituted product (5e). However, routine spectroscopic examination of (5e), expected to verify a 1,3-relationship for the larger substituents as found with the glyoxal condensations, led to the surprising discovery that the substituents were, unexpectedly, in adjacent positions. This was confirmed by n.O.e. experiments which showed an interaction between the benzotriazole-substituted methylene with the proximate methylene of the butyl group. A sequence of events which may account for this unusual substitution is suggested in Scheme 1.

A monosubstituted urea condenses reversibly with a symmetrical diketone to form an acyl imine (a) which can then cyclize to (b) (Scheme 1). Under the prevailing acidic conditions the cyclized intermediate would readily eliminate water to form a stabilized *N*-acyl iminium species[5] which in turn readily loses a proton to form a methylene imidazolone (d). This intermediate would be expected to be susceptible to attack by a nucleophile at the methylene terminus to give the final product (e). A 1,2- rather than the intuitive 1,3-substitution pattern is a consequence of the proposed mechanism. This unexpected substitution pattern is in fact observed in the formation of (5e).

The cyclic 1,2-dione cyclohexane-1,2-dione also participated in a similar manner in reactions with an *N*-alkyl-*N´*-arylurea and 1,3-dimethylthiourea to give (6a) and (6b) respectively.

While this area of chemistry served to provide an interesting variety of compounds for biological testing, none of them exhibited sufficient activity in primary agrochemical screens to warrant further investigation.



	X	R
(6a)	O	Ph
(6b)	S	Me

Experimental

Melting points were determined on a Reichert Kofler hot-stage micro-melting point apparatus and are uncorrected. Microanalyses were performed by Campbell Microanalytical Laboratory, Otago, New Zealand. Infrared spectra were recorded on a Perkin Elmer 842 spectrophotometer and refer to KBr disks. Proton n.m.r. and ^{13}C n.m.r. spectra were recorded at 200 and 50.3 MHz respectively on a Bruker AC-200 spectrometer or at 250 and 62.9 MHz on a Bruker AC250 instrument. Chemical shifts (δ) are measured in ppm. High-resolution chemical ionization mass spectra were obtained on a Jeol JMS-DX303 mass spectrometer. Low-resolution chemical ionization mass spectra were obtained on a Micromass Platform II mass spectrometer. Radial thin-layer chromatography was performed on a Harrison Research Chromatotron (7924T) using 4-mm thick silica plates (silica gel 60 PF_{254}, Merck No. 7749). Light petroleum refers to the fraction with a b.p. of 40–60°C.

trans-*1-t-Butyl-5-hydroxy-4-(*p-*tolylsulfonyl)imidazolidin-2-one (2b)*

To a mixture of hydrated sodium *p*-toluenesulfinate (2 g, 11.2 mmol) in acetic acid (3 ml) and water (5 ml) containing t-butylurea (1.16 g, 10 mmol) was added a solution of glyoxal in water (1.6 ml, 40%). The mixture was stirred at room temperature whereupon it became nearly homogeneous and then rapidly precipitated a copious amount of colourless solid. After 7 h the mixture was diluted with water (5 ml), stirred 30 min longer and then filtered and washed on the filter with water to afford the *product* as a microcrystalline colourless powder (1.61 g, 51% based on urea), m.p. 153–155°C (dec.) (Found: C, 53.8; H, 6.5; N, 9.2. $C_{14}H_{20}N_2O_4S$ requires C, 53.8; H, 6.5; N, 9.0%). ^1H n.m.r. δ ($(CD_3)_2SO$) 0.99, s, Bu^t; 2.40, s, ArC**H**$_3$; 4.41, d, *J* 2.9 Hz, CH; 5.15, d, *J* 7.7 Hz, CH; 6.69, d, *J* 7.7 Hz, OH (exch. D_2O); 7.47, d, *J* 8.0 Hz, 2H, Ar; 7.72, d, *J* 8.0 Hz, 2H, Ar; 8.03, d, *J* 2.9 Hz, NH (exch. D_2O). ^{13}C n.m.r. δ ($(CD_3)_2SO$, Bruker AC250) 21.1, 27.6, 51.7, 78.2, 79.3, 129.3, 129.8, 131.8, 145.2, 157.2.

trans-*1-(4-Ethoxyphenyl)-5-hydroxy-4-phenylsulfonylimidazolidin-2-one (2d)*

A mixture of sodium benzenesulfinate (2 g, 12.2 mmol), glyoxal (1.6 ml, 40% aq.), 4-ethoxyphenylurea (1.8 g, 10.0 mmol) and water (5 ml) in acetic acid (9 ml) was stirred for 4 days, diluted with water (20 ml) and stirring continued until crystallization was complete. The product was collected by filtration to give a single regioisomer as a colourless powder (2.1 g, 57%) (decomposes upon attempted recrystallization), m.p. 149–150°C. ^1H n.m.r. δ ($(CD_3)_2SO$) 1.29, t, *J* 6.9 Hz, CH_3; 3.95, q, *J* 6.9 Hz, 2H, CH_2; 4.80, s, 1H, CH; 5.45, s, 1H, CH; 6.80, d, *J* 8.4 Hz, Ar; 6.99, d, *J* 8.4 Hz, Ar; 7.63–7.93, m, 5H, Ar; 8.61, br s, 1H, NH. ^{13}C n.m.r. δ ($(CD_3)_2SO$) 14.6, 63.1, 77.6, 80.7, 114.2, 123.5, 129.3, 129.5, 130.1, 134.6, 134.7, 156.0. Mass spectrum *m/z* 363.3.

*1-t-Butyl-4-(*p-*tolylsulfonyl)-1,3-dihydroimidazol-2-one (3b)*

To a solution of hydrated sodium *p*-toluenesulfinate (2 g, 11.2 mmol) in formic acid (3 ml, 98%) was added a solution of glyoxal in water (1.6 ml, 40%) followed by t-butylurea (1.16 g, 10.0 mmol). The homogeneous solution was warmed at 80°C for 5 min, whereupon a mass of colourless crystals separated, and then left to cool to room temperature. The mixture was diluted with aqueous ethanol (10 ml, 50%), stirred for 2 h and the precipitate collected by filtration to give the *product* as colourless needles (2.1 g, 82%), m.p. 232–234°C (Found: C, 56.8; H, 6.1; N, 9.4. $C_{14}H_{18}N_2O_3S$ requires C, 57.1; H, 6.2; N, 9.5%). ^1H n.m.r. δ ($CDCl_3$) 1.56, s, 9H, Bu^t; 2.40, s, 3H, $ArCH_3$; 7.05, s, 1H, CH; 7.28, d, *J* 8.4 Hz, Ar; 7.88, d, *J* 8.4 Hz, Ar; 11.58, br s, 1H, NH. ^{13}C n.m.r. δ ($CDCl_3$) 21.6, 28.0, 56.5, 116.1, 120.3, 127.7, 129.9, 137.5, 144.6, 153.9.

*1-Ethyl-4-(*p-*tolylsulfonyl)-1,3-dihydroimidazol-2-one (3c)*

This was prepared in a similar manner from sodium *p*-toluenesulfinate (2 g, 11.2 mmol), glyoxal (1.6 ml) and ethylurea (0.88 g, 10.0 mmol) in formic acid (5 ml, 98%) at 80°C for 15 min and recrystallized from aqueous methanol gave the *product* (1.77 g, 66%) as colourless needles, m.p. 188–190°C (Found: C, 54.2; H, 5.1; N, 10.4. $C_{12}H_{14}N_2O_3S$ requires C, 54.1; H, 5.3; N, 10.5%). ^1H n.m.r. δ ($CDCl_3$) 1.36, t, *J* 7.3 Hz, CH_2C**H**$_3$; 2.44, s, CH_3; 3.76, q, *J* 7.3 Hz, C**H**$_2CH_3$; 7.03, s, CH; 7.34, d, *J* 8.4 Hz, 2H, Ar; 7.91, d, *J* 8.4 Hz, 2H, Ar; 11.32, br s, NH. ^{13}C n.m.r. δ ($CDCl_3$) 14.5, 21.6, 38.8, 117.7, 121.3, 127.6, 130.0, 137.5, 144.7, 153.8.

1-(4-Ethoxyphenyl)-4-phenylsulfonyl-1,3-dihydroimidazol-2-one (3d)

The compound was prepared from 4-ethoxyphenylurea (1.8 g, 10.0 mmol), glyoxal (1.6 ml, 40%) and sodium benzenesulfinate in formic acid (10 ml, 98%) at 80°C for 15 min and recrystallized from methanol to give the *product* (1.94 g, 56%), m.p. 204–206°C (Found: C, 59.1; H, 4.5; N, 8.3. $C_{17}H_{16}N_2O_4S$ requires C, 59.3; H, 4.7; N, 8.1%). ^1H n.m.r. δ ($CDCl_3$) 1.42, t, *J* 6.9 Hz, CH_3; 4.04, d, *J* 6.9 Hz, CH_2; 6.86, m, 2H, Ar; 7.23, s, 1H, Ar; 7.40–8.01, m, 6H, Ar; 11.45, br s, NH. ^{13}C n.m.r. δ ($CDCl_3$) 14.7, 63.8, 115.1, 118.2, 121.6, 124.3, 127.7, 128.1, 129.4, 133.8, 140.0, 152.8, 158.2.

*1,3-Dimethyl-4-(*p-*tolylsulfonyl)-1,3-dihydroimidazolo-2-thione (3e)*

This was obtained from the reaction between 1,3-dimethylthiourea (1.04 g, 10.0 mmol), glyoxal (1.6 ml, 40%) and sodium *p*-toluenesulfinate (2.0 g, 11.2 mmol) in formic acid (7 ml, 98%) at 80°C for 1 h. Recrystallization from methanol gave the *product* as colourless prisms (2.2 g, 70%), m.p. 131–133°C (Found: C, 49.5; H, 5.6; N, 8.9%. $C_{12}H_{14}N_2O_2S_2{\cdot}CH_3OH$ requires C, 49.7; H, 5.8; N, 8.9%). ^1H n.m.r. δ ($CDCl_3$) 2.44, s, ArC**H**$_3$; 3.41, s, 3H, C**H**$_3$OH; 3.59, s, NCH_3; 3.63, s, NCH_3; 7.35, m, 2H, Ar; 7.48, s, CH; 7.77, m, Ar. ^{13}C n.m.r. δ ($CDCl_3$/$(CD_3)_2SO$) 20.8, 32.0, 34.7, 124.6, 126.6, 126.9, 129.5, 135.7, 144.8, 166.0.

*1-t-Butyl-3-[2-oxo-1-(*p-*tolylsulfonyl)propyl]urea (4; Ar = 4-MeC$_6$H$_4$)*

A mixture of t-butylurea (0.58 g, 5.0 mmol), hydrated sodium *p*-toluenesulfinate (1 g, 5.6 mmol), water (2.5 ml) and acetic acid (3 ml) was stirred at room temperature until it became homogeneous. A solution of methylglyoxal (1 g, 40% aqueous) was added and the solution allowed to stand. The product started to separate as colourless needles within 30 min. After 6 h the mixture was diluted with 70% aqueous ethanol (5 ml), stirred for 30 min, collected by filtration and washed lightly with aqueous EtOH on the filter to give colourless needles (0.71 g, 44%). Although the *product* was colourless when freshly prepared, within a few days it had acquired a pink coloration. Attempted recrystallization led to decomposition. M.p. 155–157°C (dec.). ν_{max} 1688, 1366s cm^{-1}. ^1H n.m.r. δ ($CDCl_3$) 1.00, s, Bu^t; 2.34, s, ArC**H**$_3$; 2.53, s, CH_3; 5.90, d, *J* 9.51 Hz, CH (exch. D_2O); 6.88, d, *J* 9.51 Hz, NH (exch. D_2O); 7.26, d, *J* 8.05 Hz, 2H, Ar; 7.73, d, *J* 8.05 Hz, 2H, Ar. ^{13}C n.m.r. δ ($CDCl_3$) 21.7, 28.8, 31.1, 50.2, 75.4, 129.77, 129.80, 133.4, 145.6, 153.6, 197.6. High-resolution mass spectrum (Found: *m/z*, 327.1362. Calc. for $C_{15}H_{23}N_2O_4S$: *m/z*, 327.1378).

*4-Ethyl-5-[1-(*p-*tolylsulfonyl)ethyl]-1,3-dihydroimidazol-2-one (5a)*

A mixture of hydrated sodium *p*-toluenesulfinate (2 g,11.2 mmol), urea (0.64 g, 13.9 mmol) and hexane-3,4-dione (1.14 g, 8.9 mmol) in aqueous formic acid (9 ml, 45%) was stirred at room temperature for 2 h and then warmed to 80°C and held at this temperature for 4 h, during which time the distinct yellow colour of the diketone disappeared. The solution was cooled to room temperature, diluted with water (2 ml), stirred until compound began to precipitate and a further portion of water (2 ml) added. After 4 h the *precipitate* (1.69 g, 57%) was collected

and recrystallized from acetonitrile/ether, m.p. 130–132°C (Found: C, 57.2; H, 6.0; N, 9.5. $C_{14}H_{18}N_2O_3S$ requires C, 57.1; H, 6.2; N, 9.5%). ^{1}H n.m.r. δ ($CDCl_3$) 0.79, t, *J* 7.3 Hz, CH_2CH_3; 1.67, d, *J* 7.3 Hz, $CHCH_3$; 1.78–2.05, m, CH_2CH_3; 2.40, s, $ArCH_3$; 4.04, q, *J* 7.3 Hz, $CHCH_3$; 7.29, d, *J* 8.0 Hz, 2H, Ar; 7.62, d, *J* 8.0 Hz, 2H, Ar; 9.22, br s, NH; 10.32, br s, NH. ^{13}C n.m.r. δ ($CDCl_3$) 12.2, 12.6, 16.9, 21.6, 56.6, 109.6, 125.4, 128.8, 129.7, 133.7, 145.1, 155.0.

*1,3,4-Trimethyl-5-(*p*-tolylsulfonylmethyl)-1,3-dihydroimidazol-2-one (5b)*

This was recrystallized from aqueous methanol, m.p. 86–87°C (Found: C, 56.8; H, 6.5; N, 9.5. $C_{14}H_{18}N_2O_3S$ requires C, 57.1; H, 6.2; N, 9.5%). ^{1}H n.m.r. δ ($CDCl_3$) 1.60, s, CH_3; 2.43, s, $ArCH_3$; 3.05, s, NCH_3; 3.12, s, NCH_3; 4.10, s, CH_2; 7.31, d, *J* 8.0 Hz, 2H, Ar; 7.63, d, *J* 8.0 Hz, 2H, Ar. ^{13}C n.m.r. δ ($CDCl_3$) 8.3, 21.6 (2×C), 27.6, 52.0, 105.8, 121.1, 128.5, 129.9, 134.7, 145.3, 153.2.

*4-Methyl-5-(*p*-tolylsulfonylmethyl)-1,3-dihydroimidazolo-2-thione (5c)*

This was obtained from the reaction between thiourea (0.76 g, 10.0 mmol), butane-2,3-dione (0.86 g, 7.3 mmol) and hydrated sodium *p*-toluenesulfinate (2 g, 11.2 mmol) in formic acid (7 ml, 98%) at room temperature for 6 days. The *product* (1.88 g, 70%) was recrystallized from aqueous methanol–ethyl acetate, m.p. 260–262°C (Found: C, 49.4; H, 4.2; N, 10.6. $C_{11}H_{12}N_2O_2S_2$ requires C, 49.2; H, 4.5; N, 10.4%). ^{1}H n.m.r. δ ($(CD_3)_2SO$) 1.47, s, CH_3; 4.26, s, CH_2; 7.61, m, 5H, Ar. ^{13}C n.m.r. δ ($(CD_3)_2SO$) 7.9, 51.1, 112.0, 125.7, 128.2, 129.4, 134.2, 137.8, 160.1.

*2-[1-(5-Ethyl-2-oxo-2,3-dihydro-1*H*-imidazol-4-yl)ethyl-2-sulfanyl]propionic Acid (5d)*

This was isolated from the reaction between urea (0.6 g, 10.0 mmol), hexane-3,4-dione (1.14 g, 8.9 mmol) and 2-mercaptopropionic acid (1.06 g, 10.0 mmol) in formic acid (6 ml, 98%) for 7 days as a 1 : 1 mixture of diastereoisomers (1.53 g), isomer *A* and isomer *B*. This was recrystallized from aqueous methanol, m.p. 195–196°C (Found: C, 49.2; H, 6.4; N, 11.6. $C_{10}H_{16}N_2O_3S$ requires C, 49.2; H, 6.6; N, 11.5%). ^{1}H n.m.r. δ ($CDCl_3$) 0.43, m, 2×CH_3, isomer *A* and *B*; 0.59, d, *J* 7.3 Hz, CH_3, *A*; 0.70, d, *J* 6.9 Hz, CH_3, *B*; 0.74, d, *J* 6.9 Hz, CH_3, *B*; 0.81, d, *J* 7.3 Hz, CH_3, *A*; 1.67, m, 2×CH_2CH_3, *A* and *B*; 2.31, q, *J* 7.3 Hz, CH, *A*; 2.55, q, *J* 6.9 Hz, CH, *B*; 3.36–3.48, m, 2×CH, *A* and *B*; 9.35, m, 4×NH, *A* and *B*. ^{13}C n.m.r. δ ($CDCl_3$) (isomer *A* and *B*) 13.4, 13.7, 16.5, 16.7, 17.6, 19.4, 19.8, 33.3, 34.1, 38.7, 40.0, 115.8, 116.1, 119.6, 120.6, 154.5, 154.7, 174.0, 174.6.

5-Benzotriazol-1-ylmethyl-1-butyl-4-methyl-1,3-dihydroimidazol-2-one (5e)

This was isolated from the condensation between butylurea (1.2 g, 10.3 mmol), benzotriazole (1.6 g, 13.4 mmol) and butane-2,3-dione (0.86 g, 10.0 mmol) in formic acid (7 ml, 98%) during 7 days. Recrystallization from aqueous methanol–ethyl acetate gave the *product* (0.97 g, 33%) m.p. 139–140°C (Found: C, 62.9; H, 6.6; N, 24.6. $C_{15}H_{19}N_5O$ requires C, 63.1; H, 6.7; N, 24.5%). ν_{max} 1614, 2957, 2871s cm^{-1}. ^{1}H n.m.r. δ ($CDCl_3$) 0.77, m, CH_3; 1.17, m, $CH_2CH_2CH_2CH_3$; 2.30, s, CH_3; 3.47, m, $CH_2CH_2CH_2CH_3$; 5.63, s, CH_2N; 7.40, m, 3H, Ar; 8.05, m, 1H, Ar; 10.66, br s, NH. ^{13}C n.m.r. δ ($CDCl_3$) 9.8, 13.6, 19.8, 31.5, 41.2, 41.9, 109.2, 111.2, 117.9, 120.2, 124.2, 127.8, 132.4, 146.3, 154.0.

*1-(4-Ethoxyphenyl)-5-methyl-4-(*p*-tolylsulfonylmethyl)-1,3-dihydroimidazol-2-one (5f)*

This was obtained from 4-ethoxyphenylurea (1.8 g, 10.0 mmol), butane-2,3-dione (0.86 g, 10.0 mmol) and hydrated sodium *p*-toluenesulfinate (2 g, 11.2 mmol) in formic acid (7 ml, 98%) at 80°C for 2 h. Recrystallization from aqueous methanol gave the *product* (2.13 g, 55%), m.p. 244–245°C (Found: C, 62.2; H, 5.5; N, 7.5. $C_{20}H_{22}N_2O_4S$ requires C, 62.2; H, 5.7; N, 7.3%). ^{1}H n.m.r. δ ($(CD_3)_2SO$) 1.26, s, CH_3; 1.34, t, *J* 7.0 Hz, CH_2CH_3; 2.41, s, $ArCH_3$; 4.03, q, *J* 6.9 Hz, CH_2CH_3; 4.33, s, CH_2SO_2; 6.92–7.07, m, 4H, NAr; 7.44, d, *J* 8.0 Hz, 2H, SO_2Ar; 7.67, d, *J* 8.0 Hz, 2H, SO_2Ar; 10.02, br s, NH. ^{13}C n.m.r. δ (Bruker AC250 MHz spectrometer, $(CD_3)_2SO$) 8.5, 14.6, 21.1, 52.1, 63.3, 105.0, 114.6, 120.5, 127.4, 128.3, 128.8, 129.7, 135.0, 144.6, 152.6, 157.7.

3-Methyl-1-phenyl-4-phenylsulfonyl-1,3,4,5,6,7-hexahydrobenzimidazol-2-one (6a)

A mixture of sodium benzenesulfinate (1.8 g, 11.0 mmol), cyclohexane-1,2-dione (1.1 g, 9.8 mmol) and 1-methyl-3-phenylurea (1.5 g, 11.2 mmol) in formic acid (10 ml, 98%) was reacted over 7 days at room temperature. The *product* (1.37 g, 44%) was recrystallized from aqueous methanol, m.p. 148–150°C (Found: C, 65.5; H, 5.5; N, 7.5. $C_{20}H_{20}N_2O_3S$ requires C, 65.2; H, 5.5; N, 7.6%). ν_{max} 2920, 1690, 1135 cm^{-1}. ^{1}H n.m.r. δ ($CDCl_3$) 1.59–2.30, m, 3×CH_2; 3.33, s, CH_3; 4.18, d, *J* 5.1 Hz, CH; 7.23–7.46, m, 5H, Ar; 7.53–7.73, m, Ar; 7.86–7.91, m, 2H, Ar. ^{13}C n.m.r. δ ($CDCl_3$) 16.8, 20.1, 24.3, 28.7, 58.3, 109.6, 123.7, 126.7, 127.7, 128.9, 129.2, 129.3, 134.1, 134.5, 137.8, 153.3.

1,3-Dimethyl-4-phenylsulfonyl-1,3,4,5,6,7-hexahydrobenzimidazolo-2-thione (6b)

The crude material obtained from the reaction between cyclohexane-2,3-dione (1.1 g, 9.8 mmol), 1,3-dimethylthiourea (1.04 g, 10.0 mmol) and sodium benzenesulfinate (1.8 g, 11.0 mmol) in formic acid (6 ml, 98%) at 80°C over 6 h was purified by radial chromatography (eluent CH_2Cl_2) to afford fawn *needles* (1.2 g, 39%), m.p 169–171°C (Found: C, 56.1; H, 5.7; N, 8.6. $C_{15}H_{18}N_2O_2S_2$ requires C, 55.8; H, 5.6; N, 8.7%). ^{1}H n.m.r. δ ($CDCl_3$) 1.73–2.49, m, 3×CH_2; 3.52, s, CH_3; 3.58, s, CH_3; 4.22, d, *J* 4.75 Hz, CH; 7.54–7.74, m, 3H, Ar; 7.84–7.90, m, 2H, Ar. ^{13}C n.m.r. δ ($CDCl_3$) 16.4, 19.6, 24.2, 31.6, 33.2, 57.8, 115.4, 128.7, 129.4, 129.9, 134.2, 137.6, 163.4.

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