On the Structure of 1 : 1 Adducts of Mesoionic Compounds with Isocyanates

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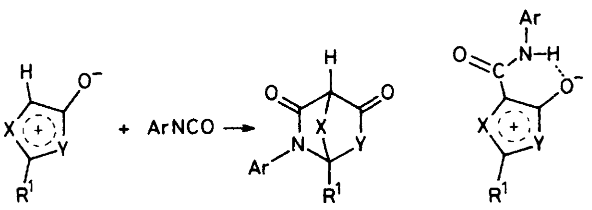
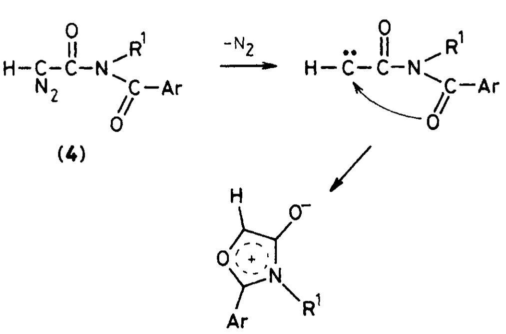
The reactions of the mesoionic species (**1**) with isocyanates yield the acylated mesoionic derivatives, formed *via* unstable cycloadducts, with thioisocyanates reacting similarly; the products of reactions between other similar mesoionic systems and isocyanates, previously described as cycloadducts, are also shown to be acylated mesoionic compounds on the basis of their physical data.

Some mesoionic compounds (**1a**—**d**) have been shown to undergo cycloaddition with isocyanates to allow isolation of 1 : 1 adducts.[1] The proposed structures are bicyclic as shown in (**2**). However, it appears that these proposed structures do not satisfy the physical properties. In the ^{1}H n.m.r. spectra, the bridgehead protons of all such adducts appear at *ca.* δ 10—12 which is at *ca.* 5—7 p.p.m. higher frequency than expected, and the fact that the protons are exchangeable with D_2O may not be accounted for by the structure (**2**). The lactams or lactones of these adducts have an absorption at 1650—1700 cm^{-1} *i.e.* at lower frequency than expected. Also, the compounds are coloured. All these data do not satisfy the structural assignment of the 1 : 1 cycloadducts (**2**) as the products, but are consistent with acylated mesoionic compounds (**3**) which could be coloured. Amide protons hydrogen bonded to the carbonyl oxygen of mesoionic system (**3**) would be expected to resonate at *ca.* δ 10 and are D_2O exchangeable. The i.r. carbonyl absorption is consistent with a mesoionic system (**3**). As described below, we have synthesised an acyl mesoionic system (**3**) *via* an unstable cycloadduct (**2**) from the reaction of (**1e**).



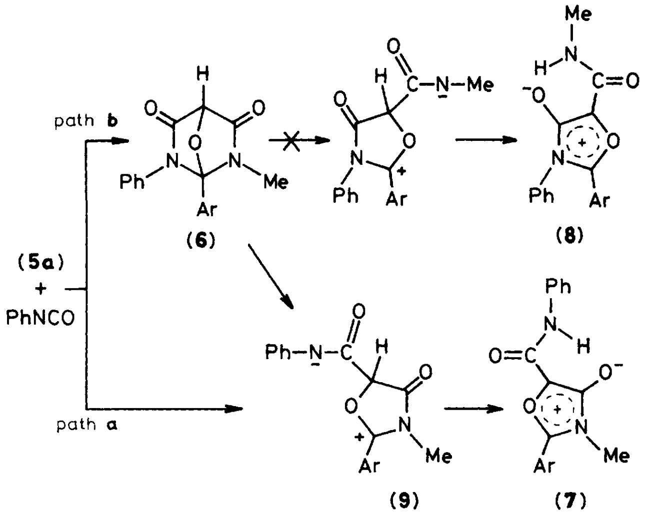
(**1**) (**2**) (**3**)

a; X = NR^2, Y = S
b; X = NR^2, Y = NR^3
c; X = NR^2, Y = O
d; X = S, Y = NR^2
e; X = O, Y = NR^2

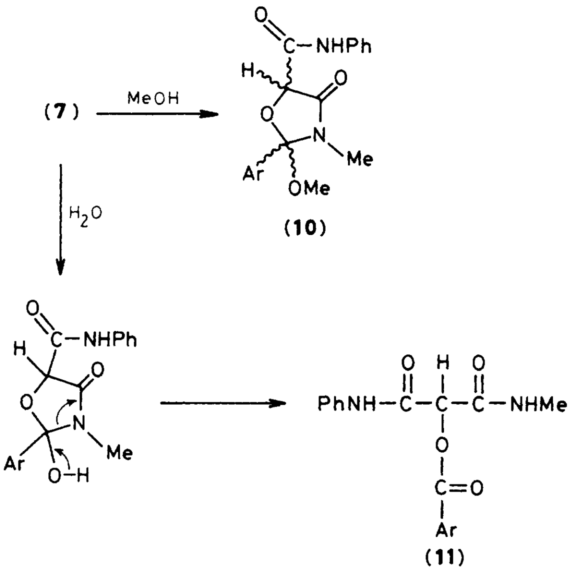


(**4**) (**5**)

a; R^1 = Me, Ar = C_6H_4Cl-*p*
b; R^1 = Ph, Ar = C_6H_4Cl-*p*
c; R^1 = Ph, Ar = Ph

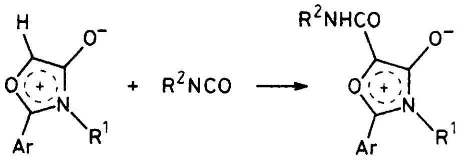


Scheme 1



We carried out the reaction of (**1e**) with isocyanates. $Cu(acac)_2$ (Hacac = acetylacetone) catalysed decomposition of (**4a**) in the presence of phenylisocyanate in benzene gave a yellow crystalline precipitate, which has the stoicheiometry of a 1 : 1 adduct of (**5a**) and phenylisocyanate. Structure (**6**) was rejected as a possibility because of the NH absorption at 3290 cm^{-1} and the amide absorption at 1670 cm^{-1} (too low for a five membered lactam) and the presence of singlets at δ 3.72 (3H) and δ 9.02 (1H) (at higher frequency than expected for a bridgehead proton of the cycloadduct). These physical data are only satisfied by the acylated mesoionic structure (**7**). Another alternative structure (**8**) would be expected to exhibit a doublet due to NMe at lower frequency. Further evidence for the product (**7**) was obtained using chemical methods. When (**7**) was dissolved in MeOH, the initial yellow colour of the solution faded and gave two isomeric 1,3 polar adducts of (**7**) with methanol, (**10**), i.r. 1725 cm^{-1} (lactam).[2] Compound (**7**) also reacted with water in dioxane to give (**11**).

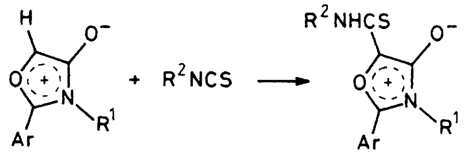
Table 1.



Ar	R¹	R²	Yield/%	M.p./°C	δ_H (NH)
p-ClC_6H_4	Me	Ph	90	187—189	9.02
p-ClC_6H_4	Me	PhCO	85	212—214	[a]
p-ClC_6H_4	Ph	Ph	11	244—245	[a]
p-ClC_6H_4	Ph	PhCO	36	237—241	[a]
Ph	Ph	Ph	33	206—210	9.12
Ph	Ph	PhCO	87	218—219	10.77

[a] Insoluble in $CDCl_3$.

Table 2.



Ar	R¹	R²	Yield/%	M.p./°C	δ_H (NH)
p-ClC_6H_4	Me	Ph	46	226—227	10.87
p-ClC_6H_4	Me	PhCO	63	219—220	[a]
p-ClC_6H_4	Ph	Ph	16	195—196	[a]
p-ClC_6H_4	Ph	PhCO	50	216—217	[a]
Ph	Ph	Ph	21	192—193	10.82
Ph	Ph	PhCO	90	208—210	[a]

[a] Insoluble in $CDCl_3$.

In a similar manner, (**4b**) and (**4c**) were treated with phenylisocyanate or benzoylisocyanate to give the corresponding acylated mesoionic compounds (Table 1).

Two mechanisms, paths (**a**) and (**b**), Scheme 1, can be considered as routes to (**7**). Path (**a**) involves direct acylation of the 5-position of (**5**) *via* (**9**). Path (**b**) involves concerted cycloaddition followed by ring opening to give (**7**). To determine which mechanism occurs, the following experiments were performed. On addition of a Pd-complex (as catalyst) to a solution of (**4a**) and phenylisocyanate in $CDCl_3$ in an n.m.r. tube, evolution of nitrogen was observed. After ten seconds, a ^1H n.m.r. spectrum showed that signals due to (**4a**) had vanished and two singlets at δ 5.02 and 2.97 in 1 : 3 ratio had appeared along with signals due to (**7**). After 30 min, the two singlets had disappeared and the signals due to (**7**) increased to an extent that corresponded to the loss of the two singlets. It seems reasonable to suppose that the singlets at δ 5.02 and 2.97 belong to the cycloadduct (**6**). This observation suggests that formation of (**7**) occurs *via* the cycloadduct (**6**), path (**b**).

In the reaction using thioisocyanates in place of isocyanates, some mesoionic compounds have also been reported to give 1 : 1 cycloadducts such as (**2**).[1a,c] However, their physical data are also not consistent with cycloaddition structures but rather acylated mesoionic compounds such as (**3**) for similar reasons as above. The reaction of (**5a**) with phenylthioisocyanate gave a brownish crystalline 1 : 1 adduct. A singlet due to NMe at high frequency (δ 3.70), a broad singlet (1H) at δ 10.87, and a carbonyl i.r. absorption at 1670 cm^{-1} are consistent with the thioacylated analogue of (**7**) instead of the corresponding analogues (**6**) or (**8**). Similarly, the reaction of (**5b**) and (**5c**) with phenylthioisocyanate and benzoylthioisocyanate also gave brownish thioacylated mesoionic species (Table 2).

Received, 21st January 1985; Com. 089

References

1 (a) K. T. Potts and S. Husain, *J. Org. Chem.*, 1972, **37**, 2049; (b) K. T. Potts, J. Baum, E. Houghton, D. N. Roy, and U. P. Singh, *ibid.*, 1974, **39**, 3619; (c) K. T. Potts, J. Baum, S. K. Datta, and E. Houghton, *ibid.*, 1976, **41**, 813.

2 M. Hamaguchi and T. Ibata, *J. Chem. Soc., Chem. Commun.*, 1980, 230.