Alkylation of Mesoionic Ring Systems with Triethyloxonium Fluoroborate

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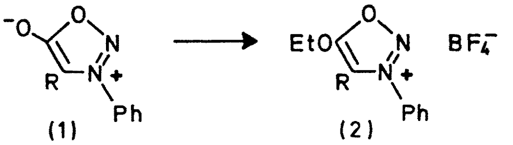
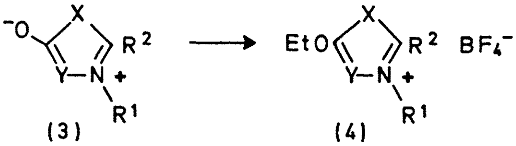
Summary Ethylation of the exocyclic oxygen atom in several five-membered mesoionic ring systems occurred readily with triethyloxonium fluoroborate.

THERE has been no report, except for the 1,2,3-triazole system,[1] that mesoionic ring systems with exocyclic oxygen atoms undergo *O*-alkylation with alkyl halides or alkyl sulphates. This failure to undergo ready alkylation is inconsistent with betaine-like character,[2] though it is not unexpected as the bond order of the carbon-oxygen bond indicates the presence of considerable double-bond character.[3] On the other hand, systems with exocyclic sulphur atoms readily undergo alkylation.[4]

We have found that alkylation at the exocyclic atom in several mesoionic ring systems occurs very readily using triethyloxonium fluoroborate.[5] Thus, 3-phenylsydnone[6] (**1**; R = H) in methylene chloride with Meerwein's reagent overnight at room temperature gave, on diluting the reaction mixture with anhydrous ether, colourless prisms (76%) from ethanol of 5-ethoxy-3-phenyl-1,2,3-oxadiazolium fluoroborate† (**2**; R = H), m.p. 68—70° [ν (N = N) 1770, ν (COC) 1200—1020 (b) cm^{-1}; u.v. max (MeOH) 280 nm, log ε 3·88; n.m.r. ($CDCl_3$) τ 8·51 (t, 3H, *J* 7·0 Hz, $-OCH_2CH_3$), 5·20 (q, 2H, *J* 7·0 Hz, $-OCH_2CH_3$), 1·98—2·50 (m, 5H, Ar*H*), 1·48 (s, 1H, 4-H)]. Similarly, 5-ethoxy-4-methyl-3-phenyl-1,2,3-oxadiazolium fluoroborate (**2**; R = Me) was obtained in 70% yield as colourless prisms, m.p. 107—109° [ν (N = N) 1775, ν (COC) 1230—1030 (b) cm^{-1}; u.v. max (MeOH) 287 nm, log ε 3·91; n.m.r. [$(CD_3)_2SO$] τ 8·66 (t, 3H, *J* 7·0 Hz, $-OCH_2CH_3$), 5·65 (q, 2H, *J* 7·0 Hz, $-OCH_2CH_3$), 7·97 (s, 3H, 4-Me), 2·24 (s, 5H, Ar*H*)] from *anhydro*-5-hydroxy-4-methyl-3-phenyl-1,2,3-oxadiazolium hydroxide[6] (**1**; R = Me). Heating of these salts above their m.p.'s regenerated the corresponding sydnone.


(1) (2)

Other mesoionic ring systems containing an exocyclic oxygen atom in a similar environment were also found to undergo ready alkylation under these conditions. Thus, *anhydro*-5-hydroxy-3-methyl-2-phenylthiazolium hydroxide[7] (**3**; R^1 = Me, R^2 = Ph, X = S, Y = CH) readily gave 5-ethoxy-3-methyl-2-phenylthiazolium fluoroborate (**4**; R^1 = Me, R^2 = Ph, X = S, Y = CH) as colourless needles (70%), m.p. 58—60° [ν (C=N) 1600, ν (COC) 1200—1010 (b) cm^{-1}; u.v. max (MeOH) 302 nm, log ε 4·08; n.m.r. [$(CD_3)_2SO$] τ 8·54 (t, 3H, *J* 7·0 Hz, $-OCH_2CH_3$), 5·98 (s, 3H, NCH_3), 5·60 (q, 2H, *J* 7·0 Hz, $-OCH_2CH_3$), 2·00—2·33 (broad s, 5H, Ar*H*), 1·83 (s, 1H, 4-H)]. *anhydro*-5-Hydroxy-3-methyl-2-phenyl-1,3,4-thiadiazolium hydroxide[8] (**3**; R^1 = Me; R^2 = Ph, X = S, Y = N) was also converted into its salt (**4**; R^1 = Me, R^2 = Ph, X = S, Y = N) which formed colourless needles (100%) from ethanol, m.p. 123—124° [ν (C=N) 1675, ν (COC) 1280—1100 (b) cm^{-1}; u.v. max (MeOH) 278 nm, log ε 4·01; n.m.r. [$(CD_3)_2SO$] τ 8·50 (t, 3H, *J* 7·0 Hz, $-OCH_2CH_3$), 5·87 (s, 3H, NCH_3), 5·29 (q, 2H, *J* 7·0 Hz, $-OCH_2CH_3$), 2·18 (m, 5H, Ar*H*)]. The mesoionic compound could be regenerated from the salt on heating it above its melting point. Similarly, 3-ethoxy-4-methyl-1-phenyl-*s*-triazolium fluoroborate (**4**; R^1 = Ph, R^2 = H, X = NMe, Y = N) was obtained as colourless needles (100%), m.p. 119—120° from *anhydro*-3-hydroxy-4-methyl-1-phenyl-*s*-triazolium hydroxide[9] (**3**; R^1 = Ph, R^2 = H, X = NMe, Y = N). Regeneration of the mesoionic compound in this case was readily effected by heat or by passing the salt over a column of alumina. The spectral characteristics of this salt [ν (C=N) 1640, 1610, ν (COC) 1250—1100 (b) cm^{-1}; u.v. max (MeOH) 248 nm, (log ε 3·98); n.m.r. [$(CD_3)_2SO$] τ 8·52 (t, 3H, *J* 7·0 Hz, $-OCH_2CH_3$), 6·28 (s, 3H, NCH_3), 5·36 (q, 2H, *J* 7·0 Hz, $-OCH_2CH_3$), 2·25 (m, 5H, Ar*H*), −0·61 (s, 1H, 5-H)] were consistent with the assigned structure.


(3) (4)

Extension of this alkylation procedure to other five-membered mesoionic systems with an exocyclic oxygen atom was equally successful. *anhydro*-4-Hydroxy-3-*p*-tolyl-1,2,3-thiadiazolium hydroxide[10] (**5**; R = *p*-$Me{\cdot}C_6H_4$) was readily converted into the corresponding salt (**6**;

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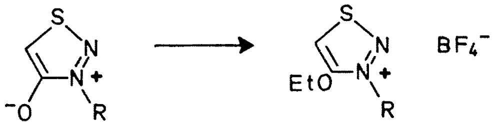
† Satisfactory analytical data were obtained for all new compounds reported.

R = *p*-Me·C_6H_4) which formed colourless plates (92%) from ethanol, m.p. 138—140° [ν (N=N) 1610, ν (COC) 1200—1010 (b) cm^{-1}; u.v. max (MeOH) 317 nm (log ε 3·94), 290 (sh) (3·73); n.m.r. [$(CD_3)_2SO$] τ 8·62 (t, 3H, *J* 7·0 Hz, $-OCH_2CH_3$), 7·58 (s, 3H, $C_6H_4{\cdot}CH_3$), 5·36 (q, 2H, *J* 7·0 Hz, $-OCH_2CH_3$), 2·16—2·60 (aromatic AB pattern, 4H, *J* 8·5 Hz), 0·76 (s, 1*H*, 5-H)].



(5) (6)

These data clearly show that alkylation occurred in all cases at the exocyclic oxygen atom. This is consistent with the protonation of 3-phenylsydnone in "super acid" solution[11] and is in agreement with recent M.O. calculations.[12] Conversion of these mesoionic systems into their salts has a pronounced effect on spectral characteristics. In particular, the chemical shifts of the ring protons undergo a large downfield shift and there is a pronounced blue shift of the long wavelength absorption band in their u.v. spectra.

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[1] M. Begtrup and C. Pedersen, *Acta Chem. Scand.*, 1966, **20**, 1555, have reported that *anhydro*-4-hydroxy-1,3-dimethyl-1,2,3-triazolium hydroxide undergoes methylation with hot methyl iodide. We have found that under comparable conditions *anhydro*-4-hydroxy-1-methyl-3-*p*-tolyl-1,2,3-triazolium hydroxide does not form the methylated product.

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