Mendeleev Commun., 1992, 2(3), 85–86

Mendeleev Communications

1-Alkyl-1,2,4-triazinium Ylides as 1,3-Dipoles in a Cycloaddition Reaction with Diethyl Acetylenedicarboxylate

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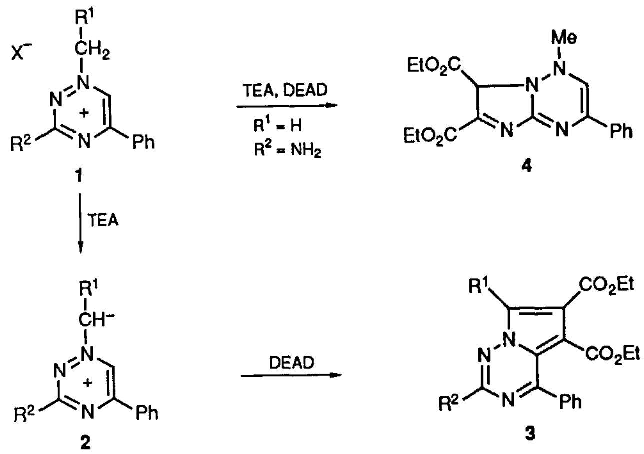
Deprotonation of 1-alkyl-5-phenyl-1,2,4-triazinium salts by triethylamine results in the formation of azomethyne ylides which undergo a 1,3-dipolar cycloaddition reaction with diethyl acetylenedicarboxylate to yield pyrrolo[2,1-*f*]1,2,4-triazines.

1,3-Dipolar cycloaddition reactions of *N*-heterocyclic ylides generated from *N*-alkylpyrydinium,[1–4] pyrimidinium[5] and other N—CH_2R substituted azinium cations bearing electron-withdrawing groups R = CN, COR′, *etc.* are well known. The ability of these ylides to react with dialkyl acetylenedicarboxylates, alkyl propiolates, maleic anhydride and other dipolarophiles has been well documented in the literature.[1–8] A few papers describe the formation of pyridinium methlides,[9–12] but no examples of cycloaddition reactions with non-stabilized 1,2,4-triazinium ylides or other *N*-alkylazinium cations bearing no electron-withdrawing groups next to the carbanionic centre have so far been reported in the literature.

We found that deprotonation of 1-alkyl-5-phenyl-1,2,4-triazinium salts **1** with triethylamine (TEA) results in azomethyne ylides **2** which are capable of reacting with diethylacetylenedicarboxylate (DEAD) to form pyrrolo[2,1-*f*][1,2,4]triazines **3** in good yields (Scheme 1, Table 1). The reaction has been effectively applied to 1-ethyl-, 1-n-propyl- and 1-n-butyl-5-phenyl-1,2,4-triazinium salts bearing amino, morpholino, piperidino, methylthio or methoxy substituents at C-3 of the triazine ring (Table 1). Evidence for the formation of compounds **3** is provided by their ^1H and ^{13}C NMR spectroscopic data.†

The reaction of 3-amino-1-methyl-5-phenyl-1,2,4-triazinium iodide **1i** with DEAD under the same conditions resulted in the



a; $R^1 = Me, R^2 = NH_2, X = BF_4$
b; $R^1 = Et, R^2 = NH_2, X = I$
c; $R^1 = Pr^n, R^2 = NH_2, X = I$
d; $R^1 = Me, R^2 = \text{piperidino}, X = BF_4$
e; $R^1 = Me, R^2 = \text{morpholino}, X = BF_4$
f; $R^1 = H, R^2 = \text{morpholino}, X = BF_4$
g; $R^1 = Me, R^2 = SMe, X = BF_4$
h; $R^1 = Me, R^2 = OMe, X = BF_4$
i; $R^1 = H, R^2 = NH_2, X = I$

Scheme 1

Table 1 Synthesis of condensed 1,2,4-triazines **3a–h** and **4** from 1-alkyl-1,2,4-triazinium salts and diethyl acetylenedicarboxylate

Starting compound	Reaction time/h	Product	Yield (%)	M.p./°C
1a	10	**3a**	70	207–208
1b	24	**3b**	64	152–153
1c	48	**3c**	65	122–123
1d	72	**3d**	58	114–145
1e	72	**3e**	63	128–129
1f	72	**3f**	50	103–104
1g	48	**3g**	45	122–123
1h	36	**3h**	71	109–111
1i	48	**4**	15	106–108

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† *General procedure and selected spectroscopic data* for pyrrolo[2,1-*f*][1,2,4]triazine **3a**: diethyl acetylenedicarboxylate (2.04 g, 12 mmol) was added to a suspension of 3-amino-1-ethyl-5-phenyl-1,2,4-triazinium tetrafluoroborate (2.88 g, 10 mmol) in 10 ml of absolute ethanol and then triethylamine (1.11 g, 11 mmol) was added dropwise with stirring. The reaction mixture was allowed to stand at room temperature for 24 h to deposit a yellow crystalline product which was collected by filtration and recrystallized from ethanol to yield 2.57 g (70%) of 2-amino-5,6-diethoxycarbonyl-7-methyl-4-phenylpyrrolo[2,1-*f*] [1,2,4]triazine **3a** as yellow needles with m.p. 207–208 °C.

^1H NMR ($CDCl_3$): δ 0.97 (t, 3H, OCH_2CH_3), 1.32 (t, 3H, OCH_2CH_3), 2.70 (s, 3H, CH_3), 3.76 (q, 2H, OCH_2), 4.31 (q, 2H, OCH_2), 4.95 (br. s, 2H, NH_2), 7.3–7.8 (m, 5H, Ph). ^{13}C NMR ($CDCl_3$): δ 10.21 (C_7—CH_3), 13.61 and 14.13 (two OCH_2—CH_3), 60.69 and 61.36 (two OCH_2), 114.13, 114.79 and 116.58 (C-5, C-6 and C-4a), 128.17 and 128.42 (C-2′, C-6′, C-3′ and C-5′ of Ph), 130.76 (C-4′ of Ph and C-7), 136.22 (C-1′ of Ph), 155.36 (C-2), 163.64 (C-4), 163.78 and 165.13 (C=O of two CO_2Et groups).

formation of 6,7-diethoxycarbonyl-1-methyl-3-phenyl-1,7-dihydro-7*H*-imidazo[1,2-*b*][1,2,4]-triazine **4** in 15% yield (Table 1). This compound exists in the C_7-H tautomeric form, as evidenced by its ^{1}H and ^{13}C NMR spectroscopic data.‡ Attempts to isolate or to obtain the corresponding pyrrolo[2,1-*f*][1,2,4]triazine have failed.

We are currently exploring further the scope and limitation of this reaction. However, the preliminary data obtained indicate that the procedure might be of synthetic value for the conversion of *N*-alkyl-1,2,4-triazinium salts and possibly other *N*-alkylazinium cations into condensed triazines and other azoloazines.

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‡ By using the double resonance decoupling technique it has been shown that in the coupled ^{13}C NMR spectrum of **4** the C_7 carbon resonance appears at δ 109.11 as a doublet with ^1J(C-7, H-7) 166.1 Hz, thus indicating that the compound exists as the C_7-H tautomer. The two coupling constants for the C-4a resonance. $^3J(C_{4\alpha}, H_7)$ 4.4 Hz and $^4J(C_{4\alpha}, NCH)$ 2.7 Hz, are also in full agreement with the structure.

^{1}H NMR sectroscopic data for 6,7-diethoxycarbonyl-1-methyl-3-phenyl-1,7-dihydro-7*H*-imidazo[1,2-*b*][1,2,4]triazine **4** ($CDCl_3$): δ 1.20 (t, 3H, OCH_2CH_3. ^3J 9.0 Hz), 1.25 (t, 3H, OCH_2CH_3, ^3J 9.0 Hz), 3.83 (s, 3H, NCH_3), 4.13 (q, 2H, OCH_2CH_2, ^3J 9.0 Hz), 4.18 (q, 2H, OCH_2CH_3, ^3J 9.0 Hz), 6.26 (s, 1H, H_7), 7.3–7.6 and 7.8–8.0 (m, 5H, Ph), 8.01 (s, 1H, H_2).

Coupled ^{13}C NMR spectrum of **4** ($CDCl_3$): δ 13.97 [q, CH_2CH_3, ^1J(C, H) 123.4 Hz], 14.06 [q, CH_2CH_3, ^1J(C, H) 123.4 Hz], 42.53 [q, NCH_3, ^1J(CH) 141.9 Hz], 59.47 [t, CH_2CH_3, ^1J(C, H) 147.9 Hz], 61.25 [t, CH_2CH_3, ^1J(C, H) 147.9 Hz], 109.11 [d, C_7, ^1J(C, H) 166.1 Hz], 128.19 [d, C_2, ^1J(C, H) 191.4 Hz], 127.78, 128.04, 132.81 and 132.91 (Ph), 149.08 (s, C_3), 149.27 (s, C_6), 158.72 [dq, $C_{4\alpha}$, $^3J(C_{4\alpha}, H_7)$ 4.4 Hz, $^4J(C_{4\alpha}, NCH_3)$ 2.7 Hz], 165.51 and 165.97 (CO of two CO_2Et groups).

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Received: Moscow, 3rd September 1991
Cambridge, 4th January 1992; Com. 1/04775B