Synthesis of 1,2-Di-*t*-butyl-6-hydroxy-1,2-dihydro-1,2,4-triazines

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Three-membered heterocycles have been known to undergo ring enlargement on reaction with compounds containing an unsaturated function or with carbanions; this process presents a versatile route to heterocycles. In general, 1,2-di-*t*-butyldiaziridinone (**1**) is not suitable for cycloaddition because of the

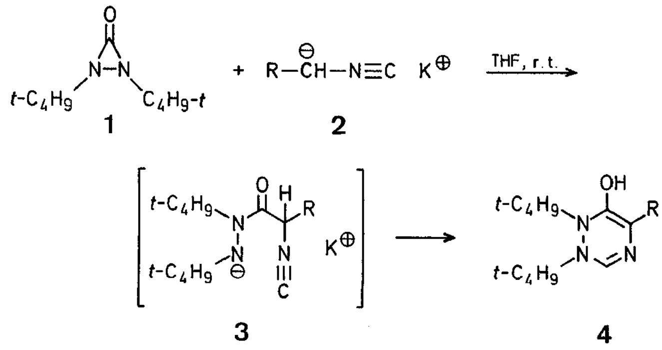

Table. 1,2-Di-*t*-butyl-6-hydroxy-1,2-dihydro-1,2,4-triazines **4a-c**

Product No.		Base	Reaction Temp./Time	Yield [%]	m.p.[a] [°C]	Molecular[b] formula	I.R. (KBr) ν [cm^{-1}]	^{1}H-N.M.R. (CDCl$_3$/TMS) δ [ppm]
4a	C_2H_5OOC	NaH	r.t./15 h	48	99–101°	$C_{14}H_{25}N_3O_3$ (283.4)	3270, 3110, 1690, 1570, 1520	0.92 (s, 9 H, *t*-C_4H_9); 1.16 (s, 9 H, *t*-C_4H_9); 1.41 (t, 3 H, $J=7.2$ Hz, CH_3); 4.39 (q, 2 H, $J=7.2$ Hz, CH_2); 5.0–5.2 (br., 1 H, OH); 7.58 (s, 1 H, HC=N)
		t-C_4H_9OK	r.t./37 h	48				
4b	C_6H_5	NaH	1. r.t./ 4 h 2. 50 °C/18 h	8	108–109°	$C_{17}H_{25}N_3O$ (287.4)	3280, 3120, 1610, 1560, 1520	0.98 (s, 9 H, *t*-C_4H_9); 1.16 (s, 9 H, *t*-C_4H_9); 3.4–3.7 (br., 1 H, OH); 7.2–8.4 (m, 5 H, C_6H_5); 7.75 (s, 1 H, HC=N)
		t-C_4H_9OK	r.t./25 h	22				
4c	H	*n*-C_4H_9Li	66 °C/7 h	25	syrup	$C_{11}H_{21}N_3O$ (211.3)	3270, 3130, 1600, 1580, 1500[c]	0.98 (s, 9 H, *t*-C_4H_9); 1.12 (s, 9 H, *t*-C_4H_9); 3.0–3.3 (br., 1 H, OH); 6.49 (s, 1 H, HC=C); 7.60 (s, 1 H, HC=N)

[a] Melting points are uncorrected.

[b] Satisfactory microanalyses obtained: C ±0.10, H ±0.14, N ±0.36.

[c] Neat.

steric hindrance of the *t*-butyl groups[1]. Earlier work in our laboratory has shown that ring enlargement of 1,2-di-*t*-butyldiaziridinone (**1**) with diphenylketene, benzoyl isocyanate, or benzonitrile in the presence of a Lewis acid gives the corresponding five-membered heterocycles[2]. Now we report the synthesis of 1,2-di-*t*-butyl-6-hydroxy-1,2-dihydro-1,2,4-triazines **4** by the reaction of 1,2-di-*t*-butyldiaziridinone (**1**) with metallated isocyanides **2**.

Treatment of **1** with metallated ethyl isocyanoacetate (**2**, R = C_2H_5OOC) at room temperature gave 1,2-di-*t*-butyl-5-ethoxycarbonyl-6-hydroxy-1,2-dihydro-1,2,4-triazine (**4a**). Starting from benzyl isocyanide or methyl isocyanide, the corresponding triazines **4** were also prepared (Table).

The triazine **4** is assumed to be formed via attack of the carbanion **2** on the carbonyl function of 1,2-*t*-butyldiaziridinone (**1**). The thus obtained intermediate **3** is subject to α-addition on the isocyanide moiety to form the triazine **4**.

1,2-Di-*t*-butyl-5-ethoxycarbonyl-6-hydroxy-1,2-dihydro-1,2,4-triazine (4a):

To a stirred solution of potassium *t*-butoxide (0.49 g, 4.4 mmol) in tetrahydrofuran (5 ml) is added dropwise ethyl isocyanoacetate (0.45 g, 4 mmol) followed by 1,2-di-*t*-butyldiaziridinone (**1**; 0.68 g, 4 mmol) in tetrahydrofuran (5 ml) at room temperature. The mixture is stirred for 37 h, and cooled to 0 °C. Water (3 ml) is added to the resultant mixture, which is extracted with ether (3 × 10 ml). The combined organic layers are washed with aqueous saturated sodium chloride solution (3 × 5 ml), and concentrated under reduced pressure. The residue is chromatographed on a silica gel column using benzene as an eluent to give the almost pure triazine **4a**, which is recrystallized from hexane; yield: 0.54 g (48%).

Received: January 14, 1982

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[2] Y. Ohshiro, M. Komatsu, Y. Yamamoto, K. Takaki, T. Agawa, *Chem. Lett.* **1974**, 383.