An Unexpected Synthesis of Enamines: (*E*)-4-Aryl-1-dialkylamino-1-butenes

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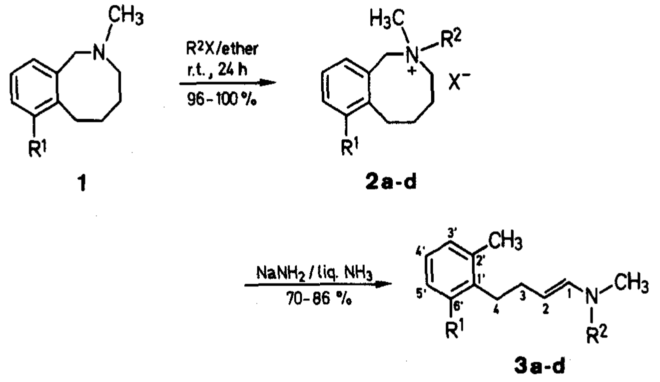
Treatment of 2,2-dialkylhexahydro-2-benzazocinium halides with sodium amide in liquid ammonia affords (*E*)-4-aryl-1-dialkylamino-1-butenes as the sole products.

Rearrangement of ammonium ylides have been the subject of many investigations in our laboratory,[1-4] especially the rearrangement of derivatives of benzazocine and benzazonine (or thienoazocine and -azonine); only the benzazoninium ylides lead mainly to azacyclophanes[3] whereas the thienoazocinium and -azoninium halides afford spiro compounds[4] upon treatment with sodium amide in liquid ammonia.

We here report the preparation of (*E*)-4-aryl-1-dialkylamino-1-butenes **3** by treatment of 2,2-dialkyl-1,2,3,4,5,6-hexahydro-2-benzazocinium halides **2** with sodium amide in liquid ammonia. The starting compounds **2** are obtained by quaternization of 2-methyl-1,2,3,4,5,6-hexahydro-2-benzazocines **1** with a suitable halide; heterocycles **1** arise from Sommelet-Hauser rearrangement of 2-aryl-1,1-dimethylpyrrolidinium halides.[5]



The *E*-configuration of the enamines **3** is established by the value of the coupling constant between the olefinic H-atoms; acid-catalysed hydrolysis to aldehydes confirms the structure of the reaction products **3**.

When the benzazocinium halide is 4,4-dimethyl-substituted, no enamine is obtained but the corresponding arylbutanal (10% yield) and 6-dimethylamino-7,7-dimethyl-6,7,8,9-tetrahydro-5*H*-benzocycloheptene (40% yield) are formed.

Table 1. 1, 2, 3, 4, 5, 6-Hexahydro-2-benzazocinium Salts **2** Prepared

2	R^1	R^2	X	Yield[a] (%)	m.p. (°C)	Molecular Formula[b]
a	H	CH_3	I	~100	253–254	$C_{13}H_{20}IN$ (317.2)
b	CH_3	CH_3	I	97	242	$C_{14}H_{22}IN$ (331.2)
c	H	C_2H_5	Br	96	216	$C_{14}H_{22}BrN$ (284.2)
d	CH_3	C_2H_5	Br	98	231	$C_{15}H_{24}BrN$ (298.3)

[a] Yield of isolated, not recrystallized product.

[b] Satisfactory microanalyses obtained: C ±0.47, H ±0.06, Br ±0.50, I ±0.26, N ±0.07.

2,2-Dialkyl-1,2,3,4,5,6-hexahydro-2-benzazocinium Halides 2a–d; General Procedure:

A mixture of the 2-methylhexahydrobenzazocine **1** (0.1 mol) and the alkyl halide (0.13 mol) in Et_2O (100 mL) is stirred at room temperature for 24 h; the precipitated ammonium salt **2** is then filtered and dried.

(*E*)-4-Aryl-1-dialkylamino-1-butenes 3a–d; General Procedure:

In a 250 mL three-necked flask equipped with a stirrer, a cooled methanol condenser, and a thermometer, a small piece of clean sodium metal is added to anhydrous liquid ammonia (100 mL) a few crystals of iron(III) nitrate hydrate are added whereon the blue color is discharged; the rest of the sodium, total: 2.3 g, 0.1 g atom) is then rapidly added. When all the sodium has been transformed, the ammonium salt **2** (0.05 mol) is added, the mixture is stirred for 10 min, and neutralized with ammonium chloride (0.1 mol). Ammonia is evaporated and the residue is washed with H_2O (20 mL) and extracted with Et_2O (3 × 30 mL). The organic layer is dried (K_2CO_3) and distilled to give the enamine **3**.

Hydrolysis of 3a; 4-(2-Methylphenyl)butanal:

A mixture of the enamine **3a** (1.89 g, 0.01 mol) and 6 normal hydrochloric acid solution (5 mL) is stirred at room temperature for 5 min,

Table 2. (*E*)-4-Aryl-1-dialkylamino-1-butenes **3** Prepared

3	Yield (%)	b.p. (°C/Torr)	Molecular Formula[a]	MS[b] *m/e* (%)	IR (neat) ν (cm^{-1})[c]	^1H-NMR ($CDCl_3$/TMS)[d] δ, *J*(Hz)	^{13}C-NMR ($CDCl_3$/TMS)[d] δ
a	86	88/0.5	$C_{13}H_{19}N$ (189.3)	189 (M^+, 1.9); 91 (4); 84 (100)	980, 1650	2.1–2.9 [m with 2s at 2.29 and 2.72, 13H, $N(CH_3)_2$, $ArCH_3$, H-3, H-4]; 4.1–4.7 (m, 1H, H-2); 5.9 (d, 1H, H-1, *J* = 13.6); 7.3 (m, 4H, H-3′, H-4′, H-5′, H-6′)	19.4 (q); 31.4 (t); 35.7 (t); 40.9 (q); 99.3 (d); 125.8 (d); 128.9 (d); 130.0 (d); 135.9 (s); 140.2 (d); 140.7 (s).
b	73	93/0.3	$C_{14}H_{21}N$ (203.3)	203 (M^+, weak); 91 (5); 84 (100)	980, 1650	1.7–3.0 [m with 2s at 2.3 and 2.7, 16H, $N(CH_3)_2$, $Ar(CH_3)_2$, H-3, H-4]; 4.1–4.6 (m, 1H, H-2); 5.9 (d, 1H, H-1, *J* = 13.6); 7.2 (m, 3H, H-3′, H-4′, H-5′)	19.9 (q); 30.0 (t); 32.1 (t); 40.9 (q); 99.2 (d); 125.4 (d); 127.9 (d); 135.9 (s); 139.2 (s); 140.2 (d).
c	70	104–106/5	$C_{14}H_{21}N$ (203.3)			1.01 (t, 3H, $NCH_2C\underline{H}_3$); 2.1–3.1 (m with 2s at 2.31 and 2.51 and q at 2.91, 12H, NCH_3, $ArCH_3$, $NC\underline{H}_2CH_3$ H-3, H-4); 4.1–4.7 (m, 1H, H-2); 5.96 (d, 1H, H-1, *J* = 13.6); 7.1 (m, 4H, H-3′, H-4′, H-5′, H-6′)	12.1 (q); 19.3 (q); 31.5 (t); 35.7 (t); 36.1 (q); 49.1 (t); 98.4 (d); 125.6 (d); 128.8 (d); 135.8 (s); 139.4 (d); 140.1 (s).
d	70	87–88/0.1	$C_{15}H_{23}N$ (217.35)			1.03 (t, 3H, $NCH_2C\underline{H}_3$); 2.1–3.1 (m with 2s at 2.33 and 2.53 and q at 2.91, 15H, NCH_3, $ArCH_3$ $NC\underline{H}_2CH_3$, H-3, H-4); 4.1–4.7 (m, 1H, H-2); 5.96 (d, 1H, H-1, *J* = 13.6); 6.98 (m, 3H, H-3′, H-4′, H-5′)	12.1 (q); 19.9 (q); 30.2 (t); 32.3 (t); 36.1 (q); 49.2 (t); 98.6 (d); 125.4 (d); 128.2 (d); 135.9 (s); 138.9 (d); 139.3 (s)

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[a] Satisfactory microanalyses obtained: C ±0.72, H ±0.16, N ±0.18.

[b] Electron-impact mass spectra obtained using a GLC quadrupole mass spectrometry system (Ribermag 10–10).

[c] Recorded on a Beckman Acculab 1 instrument.

[d] Recorded on a Bruker WP 60 or WP 80 spectrometer.

then neutralized with NaOH solution, and extracted with Et_2O (3×15 mL). The organic layer is dried ($MgSO_4$) and distilled; yield: 1.41 g (87%); b.p. 63–65 °C/20 Torr.

^{1}H-NMR ($CDCl_3$): $\delta = 1.5-2.2$ (m, 4H, H-2, H-3); 2.37 (s, 3H, Ar-CH_3); 2.54–2.67 (m, 2H, H-4); 7.18 (m, 4H_{arom}); 9.8 (t, 1H, CHO).

^{13}C-NMR ($CDCl_3$): $\delta = 19.4$ (CH_3); 22.5 (C-3); 32.4 (C-4); 43.3 (C-2); 126.0, 126.2 (C-4′, C-5′); 128.8 (C-6′); 130.3 (C-3′); 135.8 (C-2′); 139.4 (C-1′); 201.8 (C-1).

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