Novel Syntheses with Carbon Suboxide; III. Cyclocondensation with *N*-Benzylidene- or *N*-Propylidene-2-hydroxyanilines to form the Seven-Membered Ring System of 5-Benzyl(propyl)idene-4-oxido-2-oxo-2,5-dihydro-1,5-benzoxazepinium Betaines

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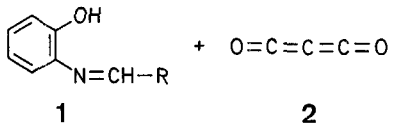
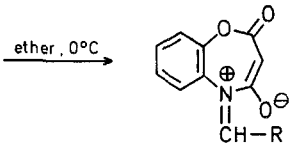
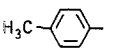
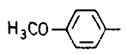
We previously showed that carbon suboxide **(2)** is a very good reagent for the synthesis of seven or eight membered heterocyclic rings with potential pharmacological activity[1,2]. Here, we report the synthesis of the previously unknown, potentially thymolectic and/or neurolectic 5-benzyl(propyl)idene-4-oxido-2-oxo-2,5-dihydro-1,5-benzoxazepinium betaines **3** from the reaction of carbon suboxide **(2)** with *N*-benzylidene-2-hydroxyanilines **1a–d** or *N*-propylidene-2-hydroxyaniline **(1e)**.



1 **2**



3

1,3	a	b	c	d	e
R					C_2H_5

All reactions were carried out using dilute diethyl ether solutions of **1** and an equimolar amount of **2**. The yields are reasonably good (Table). All the products **3a–e** exist in the mesoionic structure shown and all analytical and spectroscopic data are in agreement with the proposed structures.

5-Benzyl(propyl)idene-4-oxido-2-oxo-2,5-dihydro-1,5-benzoxazepinium Betaines 3a–e; General Procedure:

To a stirred solution of **1** (24 mmol) in dry diethyl ether (200 ml), carbon suboxide (**2**; 1.6 g, 24 mmol) is added in 2 h at 0 °C. When the addition is complete, the mixture is vigorously stirred at 0 °C for 24 h and then allowed to warm and left at room temperature for 54 h. The diethyl ether is evaporated under reduced pressure and the residue crystallized from ethanol to give **3**.

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[1] L. Bonsignore, S. Cabiddu, G. Loy, M. Secci, *J. Heterocyclic Chem.*, in press.

[2] L. Bonsignore, S. Cabiddu, G. Loy, A. M. Maccioni, *J. Chem. Soc. Chem. Commun.*, in press.

Table. 5-Benzyl(propyl)idene-4-oxido-2-oxo-2,5-dihydro-1,5-benzoxazepinium Betaines **3a–e** prepared

Product	Yield [%]	m.p. [°C]	Molecular formula[a]	I.R. (Nujol) ν [cm^{-1}]	^{1}H-N.M.R. (solvent) δ [ppm]	Mass Spectrum *m/e*
3a	70	128–130°	$C_{16}H_{11}NO_3$ (265.3)	1780–1770 (C=O); 1650 (C=N$^{\oplus}$)	(CDCl$_3$): 8.66 (s, 1H, CH=N); 8.0–6.8 (m, 10H, Ar and CH—CO)	265 (M)$^+$, 196 (M – 69)$^+$, 120 (M – 145)$^+$
3b	66	196–198°	$C_{16}H_{10}ClNO_3$ (299.7)	1780–1730 (C=O); 1620 (C=N$^{\oplus}$)	(DMSO-d_6): 7.5–6.8 (m, 10H, Ar, CH=N, and CH—CO)	299 (M)$^+$, 230 (M – 69)$^+$, 120 (M – 179)$^+$
3c	84	153–155°	$C_{17}H_{13}NO_3$ (279.3)	1780–1770 (C=O); 1650 (C=N$^{\oplus}$)	(CDCl$_3$): 7.41 (s, 1H, CH=N); 7.3–6.7 (m, 9H, Ar and CH—CO); 2.31 (s, 3H, Ar—CH$_3$)	279 (M)$^+$, 210 (M – 69)$^+$, 120 (M – 159)$^+$
3d	76	144–145°	$C_{17}H_{13}NO_4$ (295.3)	1780–1770 (C=O); 1660 (C=N$^{\oplus}$)	(CDCl$_3$): 7.4–6.5 (m, 10H, Ar, CH=N, and CH—CO); 3.73 (s, 3H, Ar—OCH$_3$)	295 (M)$^+$, 226 (M – 69)$^+$, 120 (M – 175)$^+$
3e	61	166–168°	$C_{12}H_{11}NO_3$ (217.2)	1780–1770 (C=O); 1660 (C=N$^{\oplus}$)	(CS$_2$): 7.4–6.9 (m, 6H, Ar, CH=N, and CH—CO); 3.04 (q, 2H, CH$_3$—CH$_2$); 1.13 (t, 3H, CH$_3$—CH$_2$)	217 (M)$^+$, 118 (M – 69)$^+$, 120 (M – 97)$^+$

[a] Satisfactory microanalyses obtained: C ±0.14, H ±0.09, N ±0.10.

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