REACTIONS OF AZOMETHINES AND CARBON SUBOXIDE

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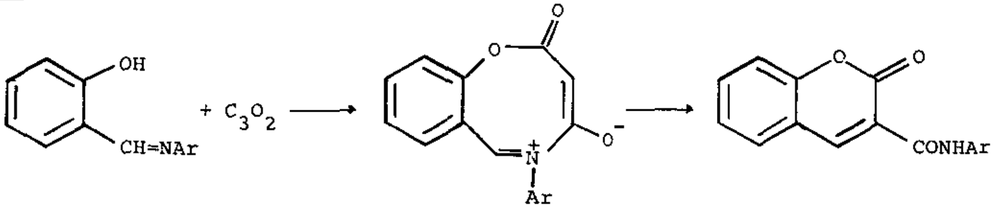
Abstract- Some reactions with azomethines and carbon suboxide are re-examined. The results show that working with very diluted and no acid diethyl ether solutions a mixture of 1,5-benzoxazocines and 2-oxo-2H-1-benzopyran-3-carboxamides is obtained.

Moving from former studies[1] and a recent literature note[2] we have re-examined some reactions of carbon suboxide (2) and azomethines (1a-c) (Scheme 1).It has been noted that, working in diethyl ether solution with traces of acid,the only products are 2-oxo-2H-1-benzopyran-3-carboxamides (4a-c)[2]. On the contrary,working in very diluted diethyl ether solution (0.065 M) in the absence of acid[3],beside the derivatives (4a-c),mesoionic compounds (3a-c) previously quoted[1] are obtained in 10-15% yields. We could isolate them only in thin-layer chromatography using silica gel GF 254 and 5:1 hexane-diethyl ether as eluent. Attempts

Scheme 1



1a-c 2 3a-c 4a-c

a: Ar = C_6H_5

b: Ar = $4\text{-}H_3C\text{-}C_6H_4$

c: Ar = $4\text{-}H_3CO\text{-}C_6H_4$

of separating 3a-c by column chromatography were unsuccessful; in this case compounds (3a-c) undergo a rearrangement with formation of 4a-c. The same occurs if 3a-c are treated, even cold, with traces of acids or if they are purified by crystallization from solvents or if they are heated beyond their melting points. It has been noted, in fact, that compounds (3a-c), which appear as yellow crystals, soon after melting at 120°C, 150°C and 170°C, respectively, solidify again at 180°C, 175°C and 195°C, respectively, as yellow needles, which melt again at 245°C, 235°C and 215°C, respectively, (mp of amides 4a-c).

Table 1. Yields, mp, IR and ^{1}H NMR Spectral Data of 3 and 4

Compd. No.	Yield (%)	mp (°C) [lit. mp (°C)]	IR ($CHCl_3$) vmax (cm^{-1})	^{1}H NMR ($CDCl_3$) δ
3a	12	120	1770 (C=O)	8.97, 8.96 (2H, each s, H-3 and H-6, interchangeables), 7.75-7.19 (9H, m, ArH).
4a	65	245 (250)[5]	3280 (N-H), 1720, 1705, 1660 (C=O)	10.18 (1H, s, NH, D_2O exchanged), 8.95 (1H, s, H-4) 7.75-7.19 (9H, m, ArH).
3b	9	150	1790 (C=O)	8.95, 8.94 (2H, each s, H-3 and H-6, interchangeables), 7.78-7.14 (8H, m, ArH), 2.28 (3H, s, CH_3).
4b	76	235 (230)[6]	3280 (N-H), 1715, 1705, 1660 (C=O)	10.19 (1H, s, NH, D_2O exchanged), 8.94 (1H, s, H-4), 7.76-7.15 (8H, m, ArH), 2.28 (3H, s, CH_3).
3c	14	170	1780 (C=O)	8.47, 8.46 (2H, each s, H-3 and H-6, interchangeables), 7.55-7.24 (8H, m, ArH), 3.71 (3H, s, OCH_3);
4c	72	215 (215-216)[7]	3290 (N-H), 1720, 1705, 1660 (C=O)	10.18 (1H, s, NH, D_2O exchanged), 8.94 (1H, s, H-4), 7.76-6.63 (8H, m, ArH), 3.75 3H, s, OCH_3).

The constitutional difference between derivatives (3a-c) and (4a-c) was pointed out by spectroscopic data (Tables 1 and 2). In fact, ir spectra of 4a-c show a characteristic NH amidic band 3290-3280 cm^{-1}, a band that does not appear in compounds

(3a-c); moreover 4a-c show a number of bands near 1720-1660 cm^{-1} characteristics of stretching vibration, ν(C=O), of α,β-unsaturated δ-lactones and of the amide carbonyl in position 3 in a δ-lactone ring[4], viceversa in the compounds (3a-c) the lactone C=O band is near 1790-1770 cm^{-1}, while the amide C=O band does not appear.
The ^{1}H nmr spectra of 4a-c show a signal of a proton bonded to an amide nitrogen near δ 10.18, signal which does not appear in the compounds (3a-c). All the mass spectra of 3a-c and 4a-c show the molecular ion. For the compounds (3a-c), moreover, formation of the fragments (M^{+} - C_3O_2) and (M^{+} - C_3O_2H) are noted, while compounds (4a-c) show the fragments (M^{+} - NHAr) and (M^{+} - CONHAr).

Table 2. Mass Spectral and Analytical Data of 3 and 4

Compd. No.	Formula	Ms m/e	Microanalyses (Calcd.) C (%)	H (%)	N (%)
3a	$C_{16}H_{11}NO_3$	265 (M^{+}), 197, 196	72.35 (72.44)	4.20 (4.18)	5.20 (5.28)
4a	$C_{16}H_{11}NO_3$	265 (M^{+}), 173, 145			
3b	$C_{17}H_{13}NO_3$	279 (M^{+}), 211, 210	73.05 (73.11)	4.61 (4.69)	4.95 (5.02)
4b	$C_{17}H_{13}NO_3$	279 (M^{+}), 173, 145			
3c	$C_{17}H_{13}NO_4$	295 (M^{+}), 227, 226	69.10 (69.14)	4.40 (4.43)	4.64 (4.74)
4c	$C_{17}H_{13}NO_4$	295 (M^{+}), 173, 145			

EXPERIMENTAL

Melting points were obtained on a Kofler hot stage apparatus, and are uncorrected.
Ir spectra were run using NaCl plates on a Perkin-Elmer 157G grating spectrophotometer as solutions in $CHCl_3$. ^{1}H Nmr spectra were recorded on a Varian FT 80A spectrometer; the δ values were obtained in $CDCl_3$ using Me_4Si as the internal standard.
Mass spectra were obtained with an "Hitachi" Perkin-Elmer RMU-6D spectrometer at 70 eV, using a direct-inlet system. Elemental analyses were carried out on a Carlo Erba model 1106 Elemental Analyzer. For thin-layer chromatography (TLC) and preparative TLC, silica gel GF 254 was used.
Literature procedures were followed in the preparation of carbon suboxide (2)[8] and azomethines (1a-c)[9].

General procedure for the preparation of 3 and 4
To a stirred solution of 1 (16 mM) in dry ether[3] (250 ml) 2 (16 mM) was added during 1 h at -70°C. When the addition was complete, the mixture was stirred at 0° for 5 h and then kept at room temperature for 48 h with stirring. The precipitate was filtered and crystallized from ethanol to give 4 as needle shaped yellow crystals.

The ether solution was evaporated in vacuo to leave a residue which was purified by preparative TLC (hexane:ether=5:1) to give 3 as tablet shaped yellow crystals. *The compound (3), after treatment with ethanol* containing traces of acetic acid, were converted into the amides (4).

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