Novel Syntheses with Carbon Suboxide; V. Cyclocondensation with 2-[(Arylimino)-methyl]benzenamines or 2-Aminobenzaldehyde Oximes to form 2-Oxo-1,2-dihydroquinoline Derivatives

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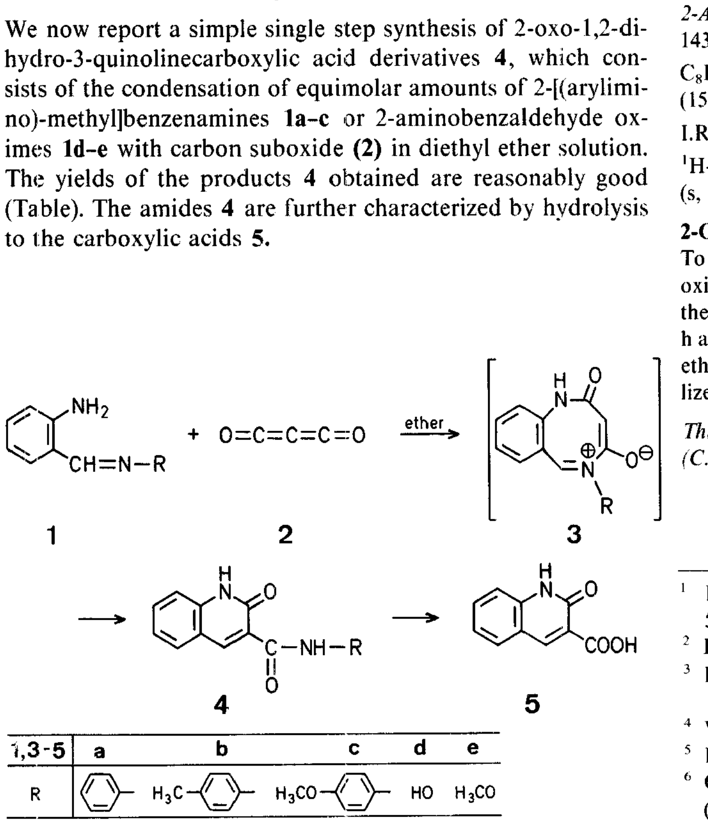
We have recently investigated the action of carbon suboxide (**2**) on appropriate substrates. For example, we have reported the reaction of this reagent with 2-[(arylimino)-methyl]phenols or 2-hydroxyaryloximes to prepare 3-substituted benzopyrones and mesoionic compounds[1,2].

We now report a simple single step synthesis of 2-oxo-1,2-dihydro-3-quinolinecarboxylic acid derivatives **4**, which consists of the condensation of equimolar amounts of 2-[(arylimino)-methyl]benzenamines **1a-c** or 2-aminobenzaldehyde oximes **1d-e** with carbon suboxide (**2**) in diethyl ether solution. The yields of the products **4** obtained are reasonably good (Table). The amides **4** are further characterized by hydrolysis to the carboxylic acids **5**.



As reported[1,2], in this case also, the compounds **4** are probably formed through rapid rearrangement reactions of the intermediates **3**, which are obtained in the first step of the reaction by the direct cycloaddition of carbon suboxide (**2**) with **1**.

The literature procedure[3] was followed for the preparation of carbon suboxide (**2**). The 2-[(arylimino)-methyl]benzenamines (**1a-c**) and the 2-aminobenzaldehyde oximes (**1d-e**) were prepared according to reported methods[4,5]. Analytical and spectral data of the new compounds **1a** and **1e** are given below.

2-[(Phenylimino)-methyl]benzenamine (1a); yield: 78%; m.p. 209–210°C (ethanol).

$C_{13}H_{12}N_2$	calc.	C 79.56	H 6.16	N 14.28
(196.3)	found	79.38	6.05	14.17

I.R. (Nujol): ν=3405, 3360 cm^{-1} (NH_2).

^{1}H-N.M.R. (Acetone-d_6/TMS): δ=8.20 (s, 1H); 7.37–6.69 (m, 9H); 5.47 ppm (s, 2H).

2-Aminobenzaldehyde O-methyloxime (1e); yield: 61%; b.p. 141–143°C/760 torr; n_D^{31} 1.6022.

$C_8H_{10}N_2O$	calc.	C 63.98	H 6.71	N 18.66
(150.2)	found	63.81	6.64	18.55

I.R. (Film): ν=3460, 3340 cm^{-1} (NH_2).

^{1}H-N.M.R. ($CDCl_3$/TMS): δ=8.13 (s, 1H); 7.25–6.55 (m, 4H); 5.33 (s, 2H); 3.86 ppm (s, 3H).

2-Oxo-1,2-dihydroquinolines (4a-e); General Procedure:

To a stirred solution of **1** (16 mmol) in dry ether (250 ml), carbon suboxide (**2**; 16 mmol) in ether (50 ml) is added in 1 h at −50°C. When the addition is complete, the mixture is vigorously stirred at 0°C for 2 h and then allowed to warm and left at room temperature for 72 h. The ether is evaporated under reduced pressure and the residue crystallized from ethanol/water to give **4**.

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Table. 2-Oxo-1,2-dihydroquinolines **4a-e** prepared

Product	Yield [%]	m.p. [°C]	Molecular formula[a] or Lit. data[b]	I.R. (Nujol) ν [cm^{-1}]	^{1}H-N.M.R. ($CDCl_3$/TMS) δ [ppm]	Mass spectra m/e
4a	95	335–336°	339°[6]	3390, 1740, 1700, 1690	9.60 (s, 1H); 8.35 (s, 1H); 8.30 (s, 1H); 7.35–6.60 (m, 9H)	264, 172, 144
4b	97	344–345°	346°[6]	3380, 1750, 1690	9.80 (s, 1H); 8.45 (s, 1H); 8.40 (s, 1H); 7.30–6.55 (m, 8H); 2.35 (s, 3H)	278, 172, 144
4c	85	289–290°	$C_{17}H_{14}N_2O_3$ (294.3)	3400, 1740, 1700, 1690	9.76 (s, 1H); 8.41 (s, 1H); 8.30 (s, 1H); 7.40–6.50 (m, 8H); 3.72 (s, 3H)	294, 172, 144
4d	75	228–230°	$C_{10}H_8N_2O_3$ (204.2)	3250, 1720, 1690	12.13 (s, 1H); 10.27 (s, 1H); 8.93 (s, 1H); 8.90 (s, 1H); 7.40–6.90 (m, 4H)	204, 172, 144
4e	68	159–160°	$C_{11}H_{10}N_2O_3$ (218.2)	3280, 1710, 1700, 1680	11.66 (s, 1H); 8.47 (s, 1H); 8.10 (s, 1H); 7.36–6.99 (m, 4H); 4.00 (s, 3H)	218, 172, 144

[a] The microanalyses were in satisfactory agreement with the calculated values: C ±0.16, H ±0.07, N ±0.1.

[b] The literature method[6] for the preparation of compounds **4a** and **4b** consists of the condensation of *o*-aminobenzaldehyde with the corresponding *N*-substituted ethyl malonoamidates.

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