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ANODIC INTRAMOLECULAR ARYLATION OF ENAMINONES+

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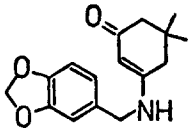
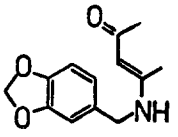
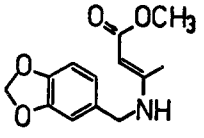
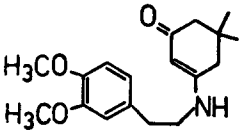
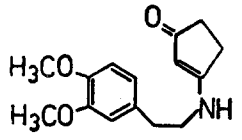
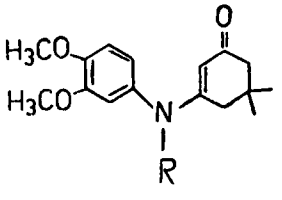
SUMMARY. N-Benzyl- and β-phenethyl-enaminones are cyclized at the anode to isoquinolines and benzazepines.

Enaminones are dimerized at the anode to 3,4-diketopyrroles[1], and arylethers to bisaryls[2]. We found that the combination of both electrophores in N-benzyl- and β-phenethyl-enaminones affords anodically isoquinolines and benzazepines. So far for these cyclizations the more elaborate *o*-bromo-arylcompounds are needed as starting materials; they are cyclized *via* arynes[3a] , photochemically[3b] , by copper(I)iodide[3c] or by palladium catalysis[3d].

The enaminones 1 - 6 were prepared by condensation of 3,4-dimethoxy- or 3,4-methylenedioxybenzylamines, -β-phenethylamines and -anilines with 1,3-diketones[4]. Their cyclovoltammetric oxidation potentials are listed in Table 1.

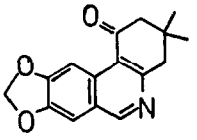
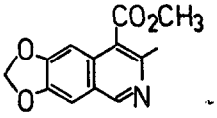
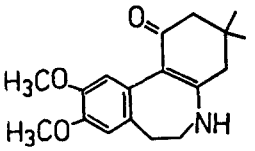
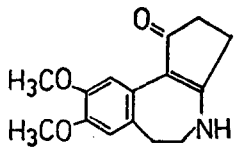
Table 1: Cyclovoltammetric peak potentials[a)] of N-benzyl-, N-β-phenethyl- and N-phenyl-enaminones (1 - 6)

Enaminone		E_p (V vs. s.c.e.)
	1	1.30, 1.60
	2	1.30, 1.55
	3	1.13, 1.50
	4	1.09, 1.32, 1.80
	5	1.25, 1.32
	6 a: R = H b: R = CH_3	a: 0.90, 1.07, 2.10 b: 1.00, 1.28, 1.65

a) Electrolyte: 0.3 M $NaClO_4$ in MeOH; undivided cell, anode: glassy carbon (1.1 cm^2), cathode: Pt-foil (1.0 cm^2), reference-electrode: s.c.e.; sweep-rate 0.04 V/s.

The first peak potential can be attributed to the oxidation of the enaminone[1], the second to this of the arylgroup[2]. The preparative electrolyses of 1, 3 - 5 lead to isoquinolines and benzazepines in fair yields (Table 2).

Table 2: Anodic[a)] cyclization of the anaminones 1, 3 - 5

Enaminone	Anode potential (V vs. s.c.e.)	Product[b)]		Yield[c)] (%)
1	+1.6		7	45 (55)
3	+1.5		8	31 (42)[d)]
4	+0.8 to +0.9		9	43 (55)
5	+1.1		10	40 (50)

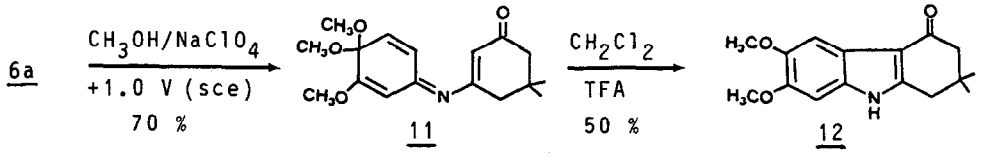
a) Electrolysis: ca. 1 mmol 1, 3 - 5 in 80 ml 0.3 M $NaClO_4$ / MeOH, undivided cell, anode, cathode: graphite, +10° C, current density: 3-4 mA/cm², current consumption: 4 F/mol.

b) The electrolyte was evaporated to dryness at 20° C, the residue dissolved in methylenedichloride, filtered and the product isolated either by recrystallization or HPLC. The spectroscopic datas of 7 and 9 were identical with those reported[3b]. 8, oil: ^1H NMR ($CDCl_3$, 270 MHz): δ 2.68 (s,3H), 4.04 (s,3H), 6.11 (s,2H), 7.17 (2s,2H), 8.92 (1H); MS (70 eV), m/e (rel. intensity) 245 (100, M^+), 214 (60), 213 (50). - 10, oil: ^1H NMR ($CDCl_3$, 270 MHz): δ 2.58 (m,4H), 2.98 (m,2H), 3.63 (m,2H), 3.84, 3.92 (6H), 5.43 (1H), 6.54 (1H), 8.06 (1H); MS (70 eV), m/e (rel. intensity) 259 (100,M^+), 244 (85). -

c) Isolated yields; numbers in parentheses: gaschromatographic yields.

d) Additionally 40 % 1-benzyl-2,5-dimethyl-3,4-di(methoxycarbonyl)-pyrrole were isolated. 2 affords under the same conditions the corresponding isoquinoline in about 2 %, the pyrrole in about 10 % yield.

6a does not cyclize in 0.3 M $NaClO_4$/MeOH as electrolyte, but forms 70 % of the iminoquinone ketal 11[5]. In a not optimized cyclization 11 yielded 50 % of the carbazol 12[6] with catalytic amounts of trifluoroacetic acid/trifluoroacetanhydride in methylenedichloride.



This anode reaction represents a convenient one-step preparation of isoquinolines and benzazepines, which can be suitable intermediates for the synthesis of lycorane[3b], Cephalotaxus[7] or erythrina[8] alkaloids.

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5) 11, brown oil: ^1H NMR ($CDCl_3$, 270 MHz) δ 6.55 (d,1H), 6.34 (d,1H), 5.68 (s,1H), 5.36 (s,1H), 3.78 (s,3H), 3.32 (s,6H), 2.33 (s,2H), 2.3 (s,2H), 1.17 (s,3H); IR (film) 1645, 1590 cm^{-1}; MS (70 eV), m/e (rel. intensity) 305 (20, M^+), 290 (40), 274 (84), 83 (100).

6) 12, yellow oil: ^1H NMR ($CDCl_3$, 270 MHz) δ 8.68 (s,1H), 7.68 (s,1H), 6.86 (s,1H), 3.95 (s,3H), 3.88 (s,3H), 2.81 (s,2H), 2.45 (s,2H), 1.16 (s,6H); MS (70 eV), m/e (rel. intensity) 273 (100, M^+), 258 (42), 217 (48), 189 (70).

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