References:

(1)- A.Guirado, F.Barba, C.Manzanera and M.D. Velasco; J.Org.Chem. 47,142 (1982)

(2)- A.Guirado, F.Barba and J.Martín; Synth. Comm. 13,327 (1983).

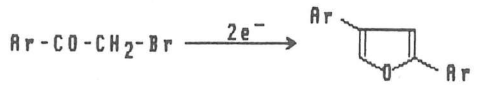
(3)- A.Guirado, F.Barba and A. Tévar; Synth. Comm. 14, 333 (1984).

(4)- L.Horner and K.Dickerhof; Chem. Ber. 116,1615 (1983).

CONTRIBUTIONS TO THE FORMATION MECHANISM OF 2,4-DIARYL FURANS AND ELECTROSYNTHESIS OF 2-ARYL-4-METHYL-FURANS.

F. Barba and J.L. de la Fuente.
Depto. Química Orgánica. Universidad de Alcalá de Henares.
Madrid. España

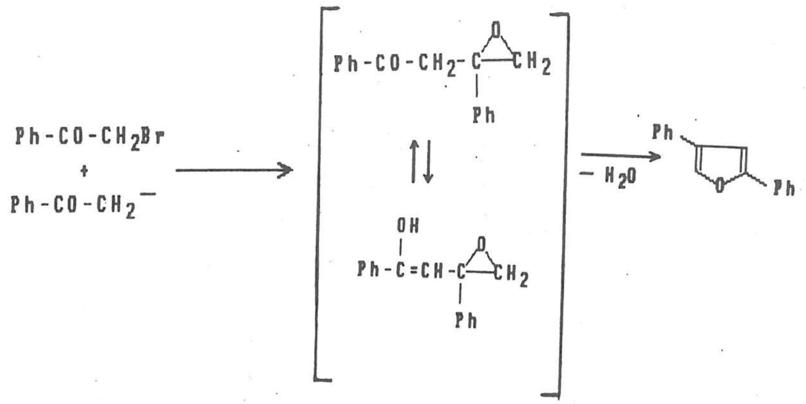
The cathodic reduction of phenacyl bromides in DMF-LiClO$_4$ leads to 2,4-diaryl furans in a very good yield(1)



The electrogenerated enolate anion reacts, with the carbonyl group of another molecule of substrate in an addition type reaction. See scheme 1.

Scheme 1.

$$Ph\text{-}CO\text{-}CH_2Br \xrightarrow{2e^-} Ph\text{-}CO\text{-}CH_2^- + Br^-$$



The postulated intermediate 3,4-epoxy-1,3-diphenyl-butan-1-one was never isolated or detected. In this paper we run the electrolysis with dibenzoyl chloro ethane as substrate, in the same conditions as before. A white solid and crystalline product was isolated (m.p=138-140ºC) and was identified as 3-benzoyl-4,5-epoxy-1,4,7-triphenyl-1,7-heptanodione in a 95%

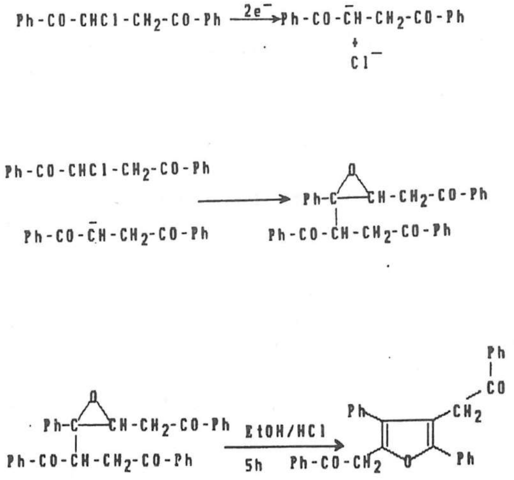
Portugaliæ Electrochimica Acta, 9 (1991) 145-148

yield. IR V_{max} (nujol mull) 3331, 1682, 1667, 1642, 1597, 1580, 1250, 1237, 718, 696 cm^{-1}.
^{1}H-NMR (CDCl$_3$) δ= 8,0-6,9 (m,20 H aromatic) and δ=5,6-2,3 (m,6H aliphatic)
Mass spectrum m/z 475(M$^+$+1)(0.1), 474 (M)(0.1), 456(2.9), 351(1.9), 133(3.7), 106(7.1), 105(100), 77(38), 51(7.1).

Its quantitative conversion to the corresponding 2,4-diaryl furan was performed by reflux in ethanol-HCl during 5h. The structure of 2,4-diphenyl-3,5-diphenacyl furan was established by mp= 161-163ºC. IR. V_{max} (nujol mull) 1698, 1597, 1580, 1493, 1449, 1327, 1213, 1181, 1003, 995, 777, 756, 748, 693, 681 cm^{-1}.
^{1}H-NMR (CDCl$_3$) δ=4.3 (S,4H -CH$_2$); δ=7.0-8.0 (m,20H aromatic)
Mass spectrum m/z 457(M$^+$+1)(3.8), 456(M)(11.5), 351(7.1), 323(3.0), 106(7.3), 105(100), 77(41,6), 51(5.7).

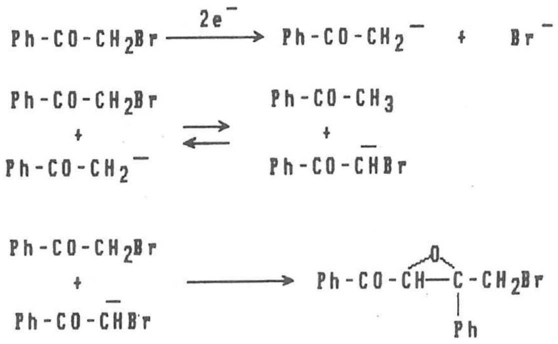
See scheme 2.

Scheme 2.

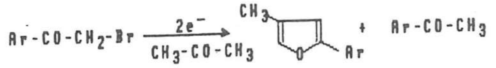


We have previously reported the influence of the substrate concentration in the cathodic reduction of phenacyl halides (2). So, the cathodic reduction of phenacyl bromide at very low concentration in DMF gives (E)-4-bromo-1,3-diphenyl-2,3-epoxy-1-butanone (48%) and acetophenone, with no furans being detected. See scheme 3.

Scheme 3.



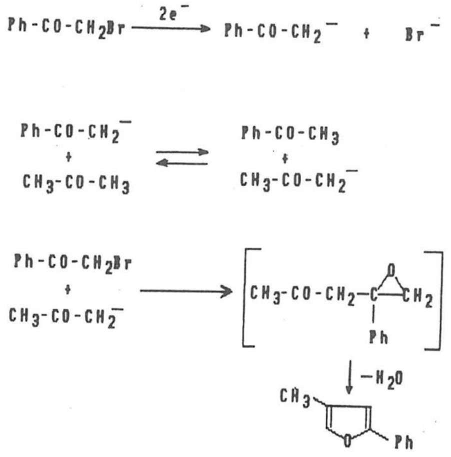
The reduction of phenacyl bromides in dry acetone-LiClO$_4$ at very low concentration of substrate leads to the corresponding 2-aryl-4-methyl-furans and acetophenones in nearly quantitative conversion.



Ar: C$_6$H$_5$, p-Cl-C$_6$H$_4$, p-H$_3$CO-C$_6$H$_4$, p-C$_6$H$_5$-C$_6$H$_4$

The logical route proposed is rationalized in scheme 4.

Scheme 4.



REFERENCES:

1.-F.Barba, M.D. Velasco and A.Guirado; Synthesis 625 (1981).

2.-F. Barba, M.D. Velasco and A.Guirado; Electrochim. Acta 28, 259 (1983).

ELECTROGENERATION OF N,O-DIAROYL-N-ARYLHYDROXYLAMINES AS PRECURSOR OF AROMATIC AMIDES.

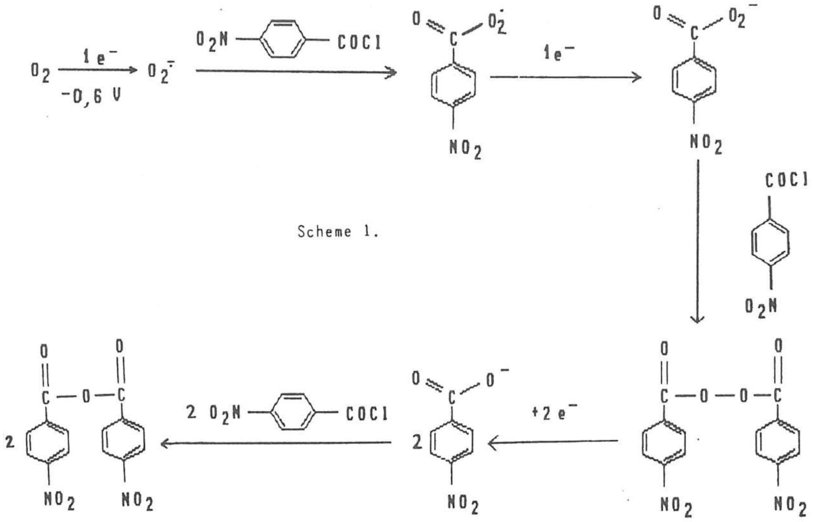
Fructuoso Barba, Jose I.Lozano and Jose Escudero.
Departamento de Química Orgánica. Universidad de Alcalá de Henares. Madrid. España

In the present paper we show the cathodic reduction of aroyl chlorides with electron-withdrawing substituens (the nitro group) in ortho- and para- positions. Both compounds behave differently as expected by other aroyl chlorides(1-5) already studied by us.

Cyclic voltammetry of 4-nitrobenzoyl chloride shows a single irreversible reduction peak at -0.60 V vs SCE and for the 2-nitrobenzoyl chloride an irreversible peak at -1.2 V vs SCE (the delocalization would be prevented).

Preparative electrolysis in an aprotic medium (dry acetone - LiClO$_4$), at controlled cathodic potential, were carried out in both cases.

When the reaction is run with the 4-nitrobenzoyl chloride in presence of oxygen, large amount of lithium 4-nitrobenzoate was formed. 4-Nitrobenzoyl peroxide was detected by TLC and the electricity consumption was 2 F mol^{-1}.



Scheme 1.

Portugaliæ Electrochimica Acta, 9 (1991) 149-152