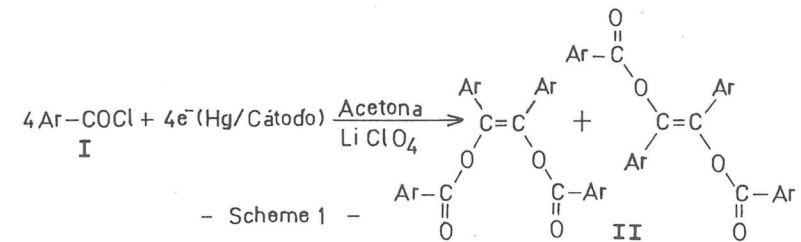


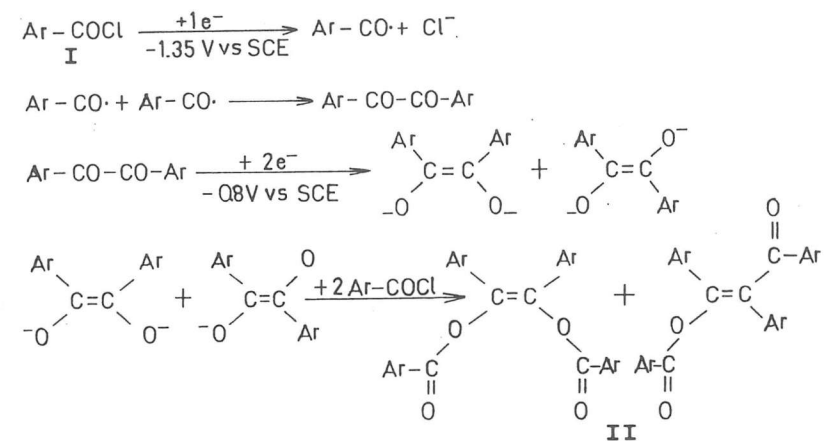
ELECTROSYNTHESIS OF DIARYLACETILENES

Carmen Polo, M<sup>a</sup> Gloria Quintanilla, Fructuoso Barba.  
Organic Chemistry Department, University of Alcalá de Henares,  
Madrid, Spain.

We have reported the cathodic reductions of several aroyl chlorides  
(1), (2).



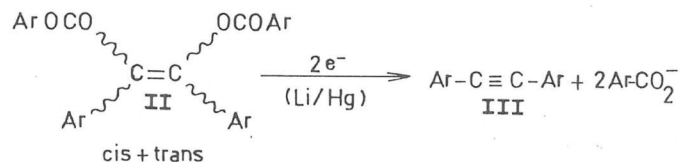
In the first step, the cleavage of the Carbon-Halogen bond generates aroyl free radicals, which dimerize leading to the corresponding diaryl-1,2-diketones. The diketones having a lower reduction potential than the starting materials undergo further reduction to form the 1,2-diaryl-1,2-ethenediolates intermediates, which are then acylated yielding the 1,2-enediol diesters (II) as final products exclusively.



- Scheme 2 -

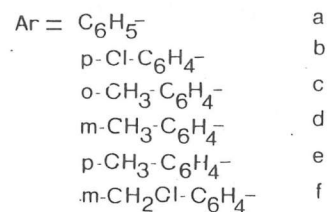
Another high yield synthesis of enediol diesters is performed by selective cathodic reduction of diaryl-1,2-diketones in the presence of acylating reagents (3).

On the other hand, L. Horner and als. (4) had transformed enediol diesters with Lithium amalgam (Li/Hg) into acetylene derivatives by "reductive elimination" according to the following equation, using two reduction equivalents.



- Scheme 3 -

In this paper we report the results of the cathodic reduction of 1,2-diaryl-1,2-enediol esters (II):



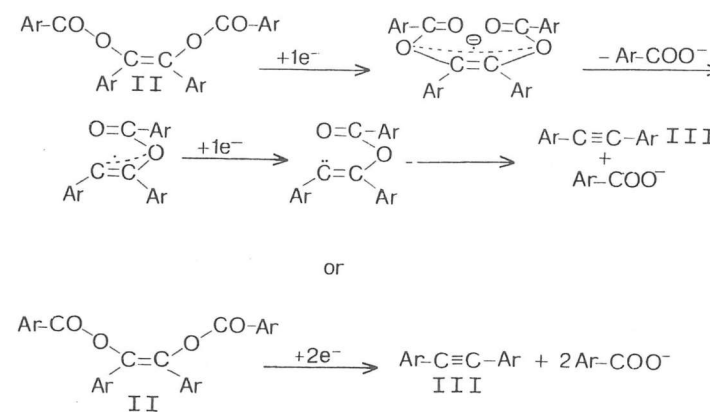
- Scheme 4 -

in order to obtain the corresponding 1,2-diarylacetylenes (III).

In our case the direct reaction starting from aroyl chlorides (I) to get (III) in the mentioned SSE (dry acetone/ LiClO<sub>4</sub>) is not possible because its discharge takes place at less negative potential (approx. -1.8V. vs SCE) than the corresponding diesters (II) (approx. -2V. vs SCE).

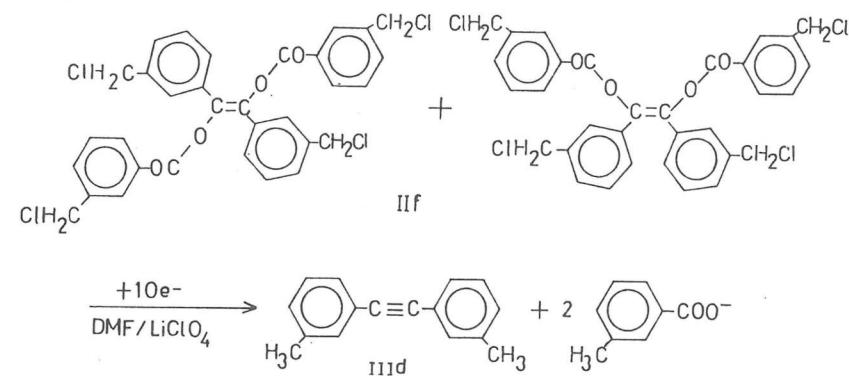
However when the enediol diesters (II) are reduced in DMF/ LiClO<sub>4</sub> as SSE (which cathodic limit is about -2.1V. vs SCE) no problems are found in the process.

The formation mechanism of 1,2-diarylacetylenes is shown in scheme 5:



- Scheme 5 -

By this procedure acetylenes (III a), (III b), (III c), (III d), (III e), are obtained. Benzilic Carbon-Chloro bond in (II f) is reduced at less negative potential than the Carbon-Oxygen one yielding the unchlorinated acetylene (III d) as shown in scheme 6. Ten electrons are involved in the process.



- Scheme 6 -

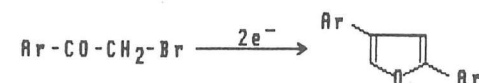
References:

- (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.

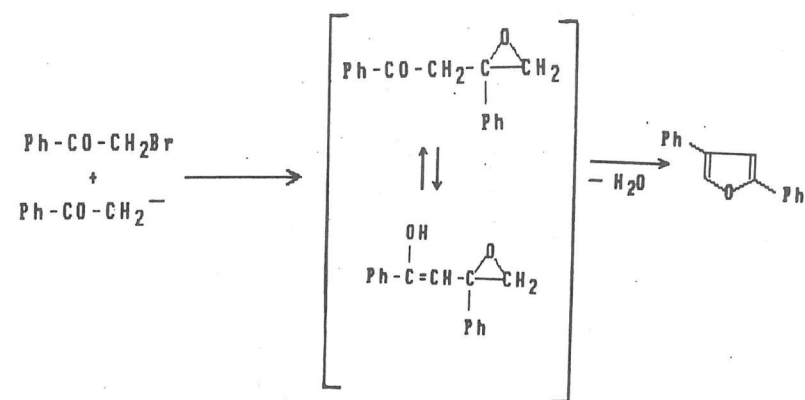
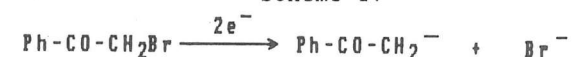
F. Barba and J.L. de la Fuente.  
 Depto. Química Orgánica. Universidad de Alcalá de Henares.  
 Madrid. España

The cathodic reduction of phenacyl bromides in DMF-LiClQ leads to 2,4-diaryl furans in a very good yield



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

Scheme 1.



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.=138-140°C) and was identified as 3-benzoyl-4,5-epoxy-1,4,7-triphenyl-1,7-heptanodione in a 95%