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ANODIC OXIDATION OF DIARYLACETYLENES AND DIARYLDIACETYLENES : ELECTROSYNTHESIS OF DIAROYL-STILBENES AND ACETYLENIC α-AND γ -DIKETONES

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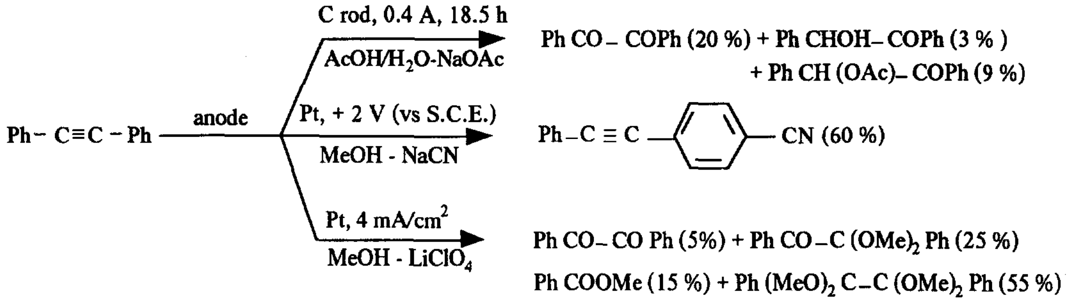
ABSTRACT : Diarylacetylenes and diaryldiacetylenes have been electrooxidized in acetonitrile through the use of a graphite plate anode, thus overcoming a very high passivation. Diarylacetylenes led mainly to 1,2-diaroyl-1,2-diaryl-ethylenes. Anodic oxidation of conjugated diaryldiacetylenes, at the same anode, led to a mixture of acetylenic α- and γ -diketones. This represents the very first synthesis of acetylenic α-diketones Ar – CO – CO – C ≡ C – Ar.

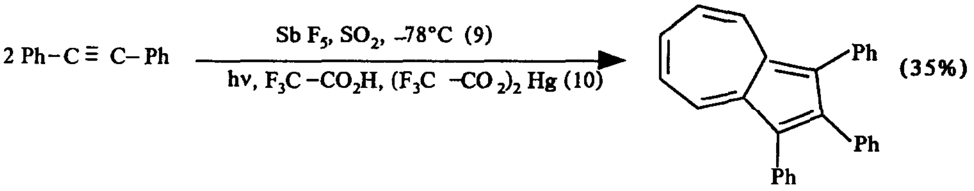
INTRODUCTION : It is known that the isolated carbon-carbon triple bond is not easily oxidized anodically. Except for acetylene, the only other alkyne whose anodic oxidation has been studied in detail is diphenylacetylene (1,2) ; but this has only been carried out in solvent-electrolyte systems :

AcOH - AcONa (3) , MeOH - NaCN (4) , MeOH - $LiClO_4$ (5),

where the electrogenerated cation radical reacts either with the electrolyte anion (AcO^-, NC^-) or with the solvent (MeOH) :



In addition various alkynes were converted to 1,2-diketones by indirect electrooxidation with ruthenium tetroxide as a mediator (6). On the other hand, in 1986 it was reported that photochemical oxidation of diphenylacetylene afforded 1,2,3-triphenyl-azulene (7). This dimerization, postulated to occur via the cation radical, allowed hope for the formation of triarylazulenes by electrochemical oxidation of diarylacetylenes in a solvent-electrolyte system, (such as MeCN - $LiClO_4$), where neither the electrolyte anion nor the solvent would react with the electrogenerated cation radical. Moreover, in the conclusion of their review of "hydrocarbon radical cations", Courtneidge and Davies (8) stated that many questions "could be probed by electrochemical methods, which as yet have been underexploited". They also point out, that the rearrangement and dimerization of arylacetylenes to give azulenes are known to take place with different Lewis acids :



The preceding prompted us to study the anodic behaviour of diarylacetylenes 1 and diaryldiacetylenes 2 for comparison of results (11) :

$\text{Ar}-\text{C}\equiv\text{C}-\text{Ar}'$

1
- a) $\text{Ar} = \text{Ar}' = \text{Ph}$
- b) $\text{Ar} = \text{Ar}' = p\text{-MeO-C}_6\text{H}_4 = \text{An}$
- c) $\text{Ar} = \text{Ph}$, $\text{Ar}' = \text{An}$

$\text{Ar}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{Ar}$

2
- a) $\text{Ar} = \text{Ph}$
- b) $\text{Ar} = \text{An}$

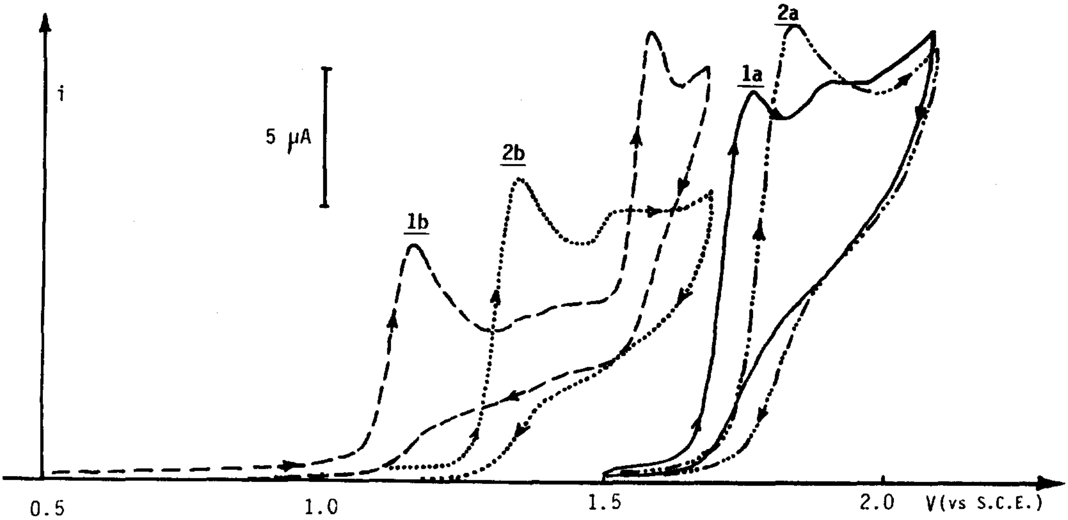
RESULTS AND DISCUSSION

CYCLIC VOLTAMMETRY : At a platinum microanode (diameter : 1 mm), in 0.1 M MeCN - Li ClO_4 as solvent-electrolyte system, at a sweep rate of 100 mV s^{-1}, diarylacetylenes 1 and diaryldiacetylenes 2 (c = 2.5 mM) exhibit irreversible oxidation peaks located at [versus a saturated calomel electrode (S.C.E.) as reference] :

Acetylenes	1 a	1 b	1 c	2 a	2 b
Epa (V)	1.74	1.17	1.37	1.84	1.35

(see figure : the voltammogram of 1c has been omitted for reasons of clarity).

After multiple sweeps, the peaks decrease to about half their height, but never disappear completely, which allowed us to hope for an anodic oxidation without passivation.



MACROSCALE ELECTROLYSES : First of all, we had to find the best electrolysis conditions.

a) Problem of passivation :

The preliminary runs were carried out on diphenylacetylene, in MeCN - $LiClO_4$. Immediately there appeared a problem of very high passivation on smooth-surfaced electrodes such as platinum or glassy carbon ; even, on a graphite rod, it was difficult for current to pass. It was only the use of a graphite plate anode which permitted this passivation to be overcome. In our opinion,that is why, up to now, diarylacetylenes have been electrolyzed only in media where either the solvent or the electrolyte anion (3,4,5) may react quickly with the electrogenerated species, thus suppressing the passivation phenomenon.

b) The effect of added base :

It is well known that acid is electrogenerated at the anode (12), as fast as the electrolysis proceeds. This acidity may be responsible for formation of tars and degradation products. To avoid such drawbacks, a soluble base such as 2,6-lutidine or an insoluble base such as K_2CO_3, is often added to the anode compartment ; details on use of these bases are given in anodic oxidations of enamines (13,14) and enol ethers (15,16). In the present case, surprisingly, addition of base resulted in lowering the yields of expected products ; so, all electrolyses were carried out in the absence of base.

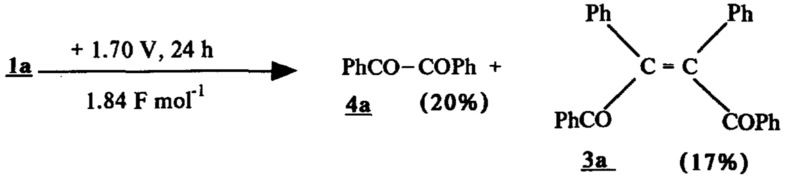
c) Choice of solvent-electrolyte system :

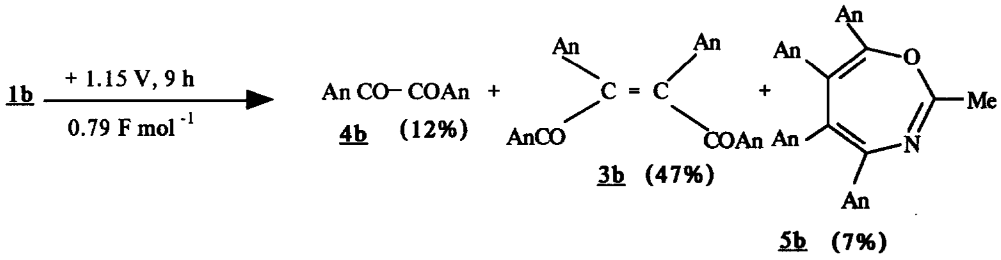
The MeCN - Li ClO_4 system is very convenient, since, during electrolysis the reaction can be followed by thin layer chromatography directly on the anolyte and because $LiClO_4$ can be simply washed away by water at the end of electrolysis. Moreover $LiClO_4$ acting as a Lewis acid, might catalyze the conversion of diarylacetylenes into triarylazulenes.

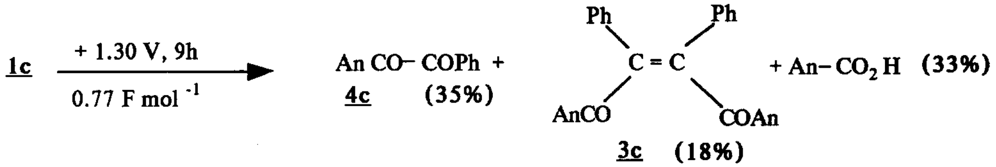
Other solvent-electrolyte systems were tested, especially CH_2Cl_2 - Bu_4NBF_4, but yields were lower.Since many cation radicals show considerable stability in trifluoroacetic acid (17), this solvent was used as a mixture (35%) with acetonitrile (with Li ClO_4 as a supporting electrolyte), but once again, yields were lower.

I - DIARYLACETYLENES

In the case of diarylacetylenes 1, the expected 1,2,3-triarylazulenes were not formed ; instead, among the electrolysis products, were isolated 1,2-diaroyl-1,2-diarylethylenes 3 [of Z configuration according to literature (21,31,33)] along with benzils 4 ; di-p-anisylacetylene 1b gave, in addition, oxazepine 5b.Unsymmetrical acetylene 1c, besides (Z)-1,2-di-p-anisoyl-1,2-diphenylethylene 3c , led to a product, with physical data closely related to 3 c (yield : 9 %), which is probably the E isomer of 3 c (but a 1-p-anisoyl-2-p-anisyl-2-benzoyl-1-phenyl-ethylene structure cannot be completely excluded) :







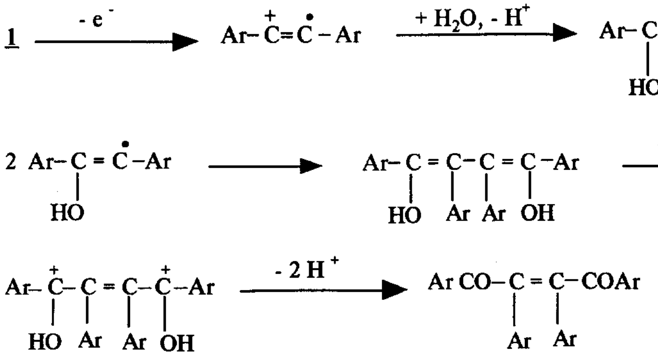
This is the first example of diaroylstilbenes 3 formed by the anodic oxidation of diarylacetylenes 1, although they are well-known products. In particular, 1,2-dibenzoyl-1,2-diphenylethylene has also been obtained by :

. electrochemical oxidation (18) or acid-catalyzed ring opening reaction of tetraphenylfuran (19)
. nitric acid oxidation of tetraphenylpyrrole (20)
. ozonolysis of tetraphenylthiophene (21)
. thermolysis or treatment with triphenylphosphine of the dimer of monothiobenzil (22).

The absence of the expected 1,2,3-triarylazulene is probably due to the instability of its cation radical (that is only if it is formed) which would give rise to degradation products.

MECHANISMS : Although the solvent-electrolyte system, MeCN - $LiClO_4$, is dried over molecular sieves beforehand, small traces of water remain, which react with the very reactive cation radicals electrogenerated in anodic reactions ; moreover, this contributes to acidification of the anolyte.

The mechanism for the formation of diaroylstilbenes 3 involves the reaction of residual water on cation radical of 1 to form an enol radical which rapidly dimerizes to a di-enol which is readily oxidized to a dication, losing two protons to lead to 3 :

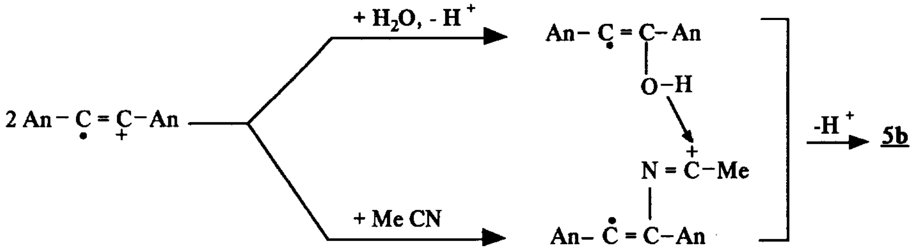


$$1 \xrightarrow{-e^-} Ar-\overset{+}{C}=\overset{\bullet}{C}-Ar \xrightarrow{+H_2O,\ -H^+} Ar-\underset{HO}{C}=\overset{\bullet}{C}-Ar$$

$$2\ Ar-\underset{HO}{C}=\overset{\bullet}{C}-Ar \longrightarrow Ar-\underset{HO}{C}=\underset{Ar}{C}-\underset{Ar}{C}=\underset{OH}{C}-Ar \xrightarrow{-2e^-}$$

$$Ar-\underset{HO}{\overset{+}{C}}-\underset{Ar}{C}=\underset{Ar}{C}-\underset{OH}{\overset{+}{C}}-Ar \xrightarrow{-2H^+} ArCO-\underset{Ar}{C}=\underset{Ar}{C}-COAr \quad 3$$

The formation of oxazepine 5b is explained by the reaction of solvent, acetonitrile, with the cation radical of 1b [electrochemical Ritter reaction : see reference (2), p. 219-236] ; the resulting nitrilium cation radical reacts with the enol radical already formed to lead to heterocycle 5b :



II - DIARYLDIACETYLENES

In the case of diaryldiacetylenes 2, a mixture of acetylenic α -diketone 6 and acetylenic γ-diketone 7 was obtained. Yields were improved by addition of 25 % dimethylformamide (DMF) to acetonitrile ; this improvement is probably due to the cleaning effect of DMF which prevents electrogenerated tars from coating the graphite plate anode, thus allowing the electrolysis to proceed smoothly. The disadvantage of the use of DMF in electrooxidation lies in the fact that, even at a fairly low potential (+1.30 V versus S.C.E.), DMF itself is oxidized,which does not permit monitoring of the electrolysis by following the decrease of electricity consumption ; thus thin layer chromatography must be used.

$$\underline{2} \xrightarrow[\text{or } 1.30\text{ V, } 90\text{ h } \underline{(2b)}]{+\,1.80\text{ V, } 30\text{ h } \underline{(2a)}} \mathrm{ArCO{-}CO{-}C{\equiv}C{-}Ar} \; + \; \mathrm{ArCO{-}C{\equiv}C{-}COAr}$$

6a : 5 %	7a : 60 %
6b : 28 %	7b : 12 %

It is worth noting that in the anodic oxidation of diarylacetylenes 1, the addition of 25 % DMF to MeCN is less favourable :

. diphenylacetylene gave only benzil 4a (51%)

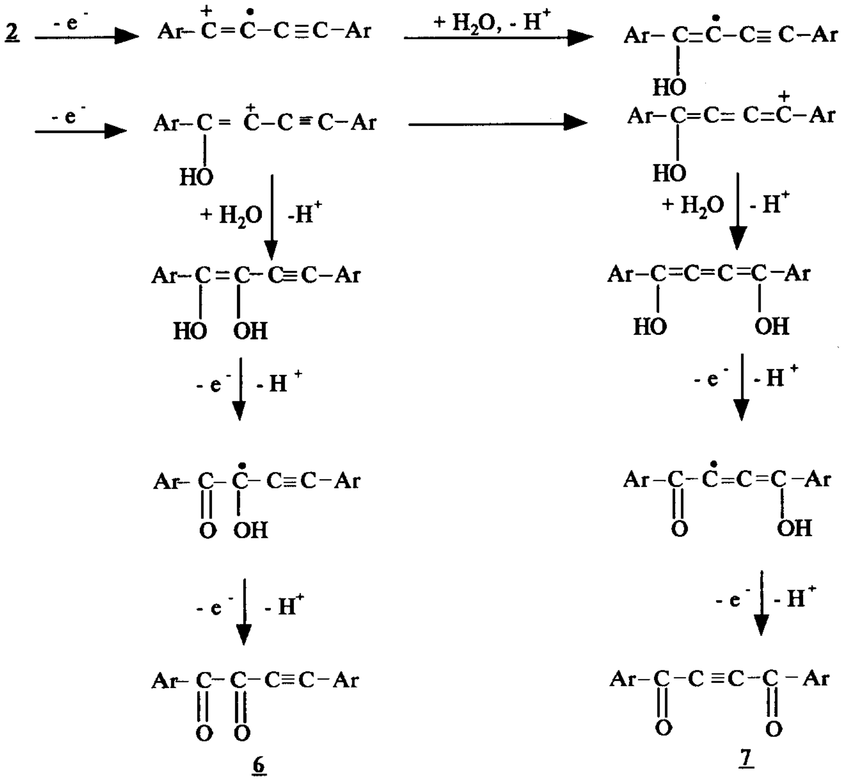
. the yield of 3b decreased from 47 % to 36 % and oxazepine 5b did not form, by oxidation of di-p-anisylacetylene.

On the other hand, the electrooxidation of commercial diphenylbutadiyne 2a giving dibenzoylacetylene 7a PhCO − C ≡ C − COPh in 60 % yield represents a good synthesis of this interesting dienophile (23). This representents the first synthesis of acetylenic α-diketones 6 which are difficult to prepare by conventional methods. It should be noted however,that derivatives of acetylenic α-diketone 6a were prepared recently (24) by photoaddition reactions of p-quinones to diphenylbutadiyne.

MECHANISMS : As in the case of diarylacetylenes 1 , the mechanism of formation of acetylenic diketones 6 and 7 from diaryldiacetylenes 2 involves the reaction of residual water on cation radical of 2 giving rise to an acetylenic enol radical which immediately loses an electron to lead to a cation in equilibrium under two tautomeric forms :

. the enyne form reacts again with residual water giving an acetylenic enediol which after two successive losses of electron and proton, finally leads to acetylenic α-diketone 6.

. the cumulene form reacts in the same way and leads to acetylenic γ-diketone 7.



CONCLUSION : This research, despite the failure to prepare triarylazulenes by anodic oxidation of diarylacetylenes, has been successful, especially on three points :

. the use of a graphite plate anode to overcome a very high passivation due probably to the inhibiting effect of electrogenerated polyacetylenes.

. the first anodic oxidation of diarylacetylenes leading chiefly to diaroylstilbenes, in the presence of the residual water of acetonitrile.

. the very first synthesis of acetylenic α-diketones by anodic oxidation of diaryldiacetylenes.

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Experimental Section

General Methods : The progress of reactions and purity of samples were checked by t.l.c. on silica gel plates (Merck n° 5714). The purification of electrolysis products was carried out by column chromatography on silica gel (Merck n° 7736). Proton n.m.r. spectra were recorded at 60 MHz, with TMS as an internal reference, in CDCl$_3$. Acetonitrile was purchased from Carlo-Erba, dried on molecular sieves (3 A) and used without further purification. Dimethylformamide was redistilled before use and stored over molecular sieves (4 A). LiClO$_4$ was purchased from Fluka and kept in a desiccator.

Starting materials : Diphenylacetylene 1a is commercial (Aldrich). Di-p-methoxyphenylacetylene 1b was prepared by reaction of triethyl phosphite on di-p-methoxybenzil (25), and p-methoxyphenyl-phenylacetylene 1c by reaction of p-iodoanisole on cuprous phenylacetylide (26). Diphenylbutadiyne 2a can be purchased from Aldrich or easily prepared according to (27). Di-p-methoxyphenylbutadiyne 2b was synthesized in a two-step procedure : preparation of p-methoxyphenylacetylene (28) which, in the presence of cupric acetate in pyridine-methanol mixture, according to the method described for 2a (27), gave 2b with 77 % yield (m.p. 144°C from methanol).

Typical procedure for anodic oxidation of acetylenes 1 :

Electrolyses were carried out in a three-compartment H-shaped cell, with an intermediate compartment (useful volume = 5 mL) to minimize mixing of catholyte (V = 30 mL) and anolyte (V = 65 mL). Compartments are separated by two glass-frits (inside diameter = 2 cm). The cathode is a graphite rod (diameter = 1 cm). The anode compartment is closed by a triple-bored silicone stopper provided with a salt bridge (in which is dipping the saturated calomel reference electrode), a connexion for the graphite plate anode (area = 4 cm x 2.5 cm, thickness = 1 cm) and a small glass tube for, possibly, bubbling inert gas (here, not utilized). A volume of 100 mL of 0.3 M MeCN – LiClO$_4$ is divided up among the three compartments and the salt bridge. Electrodes are connected with a potentiostat and a coulometer ; after a preliminary electrolysis, about 5 mmol of acetylene 1 are added, at a potential such that current intensity never exceeds 20 mA and electrolysis is carried on until intensity drops to near zero. If the electricity consumption was high, additional LiClO$_4$ was introduced in the cathode compartment, from time to time.

The anolyte is then diluted by 350 mL of dichloromethane and 250 mL of water are added.After decantation, the organic layer is washed five times with 50 mL of water and dried over anhydrous sodium sulfate. After usual work-up, the remainder is purified by column chromatography.

Anodic oxidation of diphenylacetylene 1a :

6 mmol (1.07 g) of diphenylacetylene 1a were electrooxidized for 24 hours at + 1.70 V ; the electricity consumption was 1.84 F mol^{-1}. After work-up, chromatography of the brown oil residue (1.25 g), with cyclohexane 95 - AcOEt 05 mixture as an eluent, gave :

. 0.25 g (20 %) of diphenylethanedione (benzil) 4a : yellow crystals, m.p. 95°C (methanol), lit. (29) : m.p. 95°C.
. 0.20 g (17 %) of cis 1,2,3,4-tetraphenyl-2-butene-1,4-dione 3a : colorless crystals, m.p. 215-218°C (acetone), lit. (21) m.p. 215-217°C ; IR (KBr) : ν CO 1655 ; NMR (CDCl$_3$) δ Ph 7.0 - 7.5 (m, 16 H) and 7.75 - 8.00 (m,4 H) ; MS : m/z 388 ($C_{28}H_{20}O_2$).

Anodic oxidation of bis (4-methoxyphenyl)-acetylene 1b :

5 mmol (1.19 g) of di-p-anisylacetylene 1b were electrooxidized for 9 hours at + 1.15 V ; the electricity consumption was 0.79 F mol^{-1}. After work-up, chromatography of the solid residue (1.40 g) with dichloromethane as an eluent, afforded :

. 0.165 g (12 %) of bis (4-methoxyphenyl)-ethanedione (anisil) 4b : yellow crystals, m.p. 133°C (diisopropyl ether), lit. (30) m.p. 131-133°C ; IR (KBr) ν CO 1650 ; NMR (CDCl$_3$) δ OMe 3.83 (s, 6 H), δ Ar 6.84 and 7.83 (AA' BB' system, 8 H).

. 0.60 g (47 %) of cis 1,2,3,4-tetrakis (4-methoxyphenyl)-2-butene-1,4-dione 3b : yellow crystals, m.p. 186°C (10 mL iPr$_2$O + 5 mL AcOEt), lit. (31) m.p. 184-185°C and (22) m.p. 183-184°C ; IR (KBr) νCO 1650 ; NMR (CDCl$_3$) δ OMe 3.65 (s, 6 H), 3.68 (s, 6H), δAr 6.62 and 7.67 (AA'BB' system, 8 H), 6.55 and 6.98 (AA'BB' system, 8 H) ; MS m/z 508 ($C_{32}H_{28}O_6$).

. and, after addition of 5 % AcOEt to the eluent (dichloromethane), 0.090 g (7 %) of 2-methyl-4,5,6,7-tetrakis (4-methoxyphenyl)-1,3-oxazepine 5b : colorless crystals (fluorescing in UV light), m.p. 161-162°C (8 mL iPr_2O + 1.5 mL AcOEt) ; IR (KBr) ν C = N 1645 ; NMR ($CDCl_3$) δ Me 2.20 (s, 3H), δ OMe 3.58 (s, 6 H) and 3.69 (s, 6 H) δ Ar 6.42, 6.55, 6.60, 6.75, 6.93, 7.07 and 7.40 - 7.70 (superimposed AA'BB' systems, 16 H) ; MS m/z 533 ($C_{34}H_{31}NO_5$), 492 (M-MeCN), 357, 135.

Anodic oxidation of (4-methoxyphenyl)-phenyl-acetylene 1c :

4.8 mmol (1.00 g) of p-anisyl-phenylacetylene 1c were electrooxidized for 9 hours at + 1.30 V ; the electricity consumption was 0.77 F mol^{-1}. After work-up, chromatography of the brown solid residue (1.25 g) with dichloromethane, as an eluent, afforded:

. 0.40 g (35 %) of 1-(4-methoxyphenyl)-2-phenyl-ethanedione 4c : yellow crystals, m.p. 63°C (diisopropyl ether), lit. (32) m.p. 64°C ; IR ($CHCl_3$) ν CO 1675 ; NMR ($CDCl_3$) δ OMe 3.80 (s, 3 H) δ Ar 6.81 and 7.80 (AA'BB' system) and 7.42 (peak) (9 H) ; MS m/z 240 ($C_{15}H_{12}O_3$).

. 0.10 g (9 %) of trans 1,4-bis (4-methoxyphenyl)-2,3-diphenyl-2-butene-1,4-dione 3c' : colorless crystals, m.p. 205-208°C (iPr_2O – AcOEt) ; IR (KBr) νCO 1645 ; NMR ($CDCl_3$) δ OMe 3.72 (s, 6 H) δ Ar 6.65 and 7.80 (AA'BB' system) 7.27 and 7.03 (peaks) (18 H) ; MS m/z 448 ($C_{30}H_{24}O_4$), 135 (p–MeO–C_6H_4–CO).

. 0.15 g of a mixture of unidentified products.
. 0.20 g (18 %) of cis 1,4-bis (4-methoxyphenyl)-2,3-diphenyl-2-butene-1,4-dione 3c : colorless crystals, m.p. 174°C (AcOEt) , lit. (33) m.p. 176°C ; IR (KBr) νCO 1650 ; NMR ($CDCl_3$) δ OMe 3.72 (s, 6 H), δ Ar 6.66 and 7.71 (AA'BB' system) and 7.08 (peak) (18 H) ; M.S. m/z 448 ($C_{30}H_{24}O_4$) ,135 (p–MeO–C_6H_4–CO).

. and, after addition of 10 % MeOH to dichloromethane, 0.30 g (33 %) of 4-methoxy-benzoic acid : colorless crystals, m.p. 180°C (iPr_2O - AcOEt), lit. (29, p. 3692) m.p. 184°C; IR (KBr) ν CO_2H 1670 and νOH 2540-3040; NMR ($CDCl_3$) δ OMe 3.87 (s, 3 H), δ Ar 6.87 and 7.95 (AA'BB' system, 4 H) δ CO_2H 9.17 (dome , 1 H).

Typical procedure for anodic oxidation of diaryldiacetylenes 2 :

The procedure described for anodic oxidation of diarylacetylenes 1 was used also for diaryldiacetylenes 2, except that the solvent was a mixture of acetonitrile (75 %) and dimethylformamide (25 %).The electrolysis was monitored by thin layer chromatography.

Anodic oxidation of 1,4-diphenylbutadiyne 2a :

5 mmol (1.01 g) of diphenyldiacetylene 2a were electrooxidized for 30 hours at + 1.80 V. After work-up, careful chromatography of the crystallized residue (1.20 g) with cyclohexane 95-Ac OEt 05 as an eluent, gave :

. 0.060 g (5 %) of 1,4-diphenyl-3-butyne-1,2-dione 6a : yellow gummy solid ; IR (film) ν (C ≡ C) 2195 , 2220 (shoulder) ν CO 1650, 1670 ; NMR ($CDCl_3$) δ Ph 8.00 - 8.20 (m, 2 H) and 7.25 - 7.80 (m, 8 H) ; MS m/z 234 ($C_{16}H_{10}O_2$) : according to mass spectrometry, the product was slightly contaminated, especially with PhCO–CO–CH = CH–Ph (m/z 236), but, despite a further purification by a second chromatography, impurities remained.

. 0.690 g (60 %) of 1,4-diphenyl-2-butyne-1,4-dione (dibenzoyl-acetylene) 7a : colorless crystals, m.p. 112°C (ethanol), lit. (34) m.p. 112°C (benzene) ; IR (KBr) ν (C ≡ C) invisible, on symmetrical grounds, ν CO 1640 ; NMR ($CDCl_3$) δ Ph 8.12-8.33 (m,4 H) and 7.30–7.80 (m, 6 H) ; MS m/z 234 ($C_{16}H_{10}O_2$).

Anodic oxidation of 1,4-bis (4-methoxyphenyl)-butadiyne 2b :

4 mmol (1.05 g) of di-p-anisyldiacetylene 2b were electrooxidized for 90 hours at + 1.30 V : such a duration is due to passivation (despite the graphite plate anode), requiring repeated switchings on and off at the beginning of the electrolysis. After work-up, chromatography of the dark brown oil residue (1.25 g), with dichloromethane 60-cyclohexane 40 mixture as an eluent, afforded:

. 0.335 g (28 %) of 1,4-bis (4-methoxyphenyl)-3-butyne-1,2-dione 6b : orange-yellow crystals, m.p. 99°C (diisopropyl ether) ; IR (KBr) ν (C ≡ C) 2240 (weak) 2170 and 2195 (strong), ν CO 1640 and 1655 ; NMR ($CDCl_3$) δ OMe 3.85 (s, 3 H) and 3.90 (s, 3 H) , δ Ar 6.99 and 8.08 (AA'BB' system, 4 H) and 6.90 and 7.60 (AA'BB' system, 4 H) ; MS m/z 294 ($C_{18}H_{14}O_4$), 266, 238, 223, 159, 144, 135.

. 0.185 g (12 %) 1,4-bis (4-methoxyphenyl)-2-butyne-1,4-dione (di-p-anisoylacetylene) **7b** : colorless crystals, m.p. 137°C (iPr_2O – AcOEt), lit. (34) m.p. 138°C and (35) m.p. 136-138°C ; IR (KBr) ν (C ≡ C) invisible, on symmetrical grounds, ν CO 1635, 1645 ; NMR ($CD\,Cl_3$) δ OMe 3.92 (s, 6 H), δ Ar 6.99 and 8.16 (AA'BB' system, 8 H) ; MS m/z 294 ($C_{18}H_{14}O_4$).

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