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Preparation and Photolysis of Diaryl Esters of Acetylenedicarboxylic Acid

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Key Words: esterification of acetylenedicarboxylic acid; asymmetric derivative of acetylenedicarboxylic acid; photo-Fries rearrangement; 5-exo-dig ring closure; intramolecular nucleophilic attack to acetylenic ketones

Abstract. *Two diaryl acetylenedicarboxylates 1a,b have been prepared in moderate yields by direct reaction of acetylenedicarboxylic acid with the corresponding phenols catalyzed by sulfuric or p-toluenesulfonic acids and also through acetylenedicarbonyl chloride. The accompanying by-products have been characterized. Attempted esterification using N,N'-dicyclohexylcarbodiimide as condensing agent gives an asymmetric ester amide 11a and a substituted uracil 12a. Photolysis of the aryl esters 1a,b in benzene solution affords the benzocoumaran-3-ones 14a,b. In the case of 1b, minor amounts of a polycyclic condensed 4-chromanone 17b have also been observed. These results show that the nature of the substituent attached at the β-position of the C ≡ C triple bond plays an important role in the cyclization of o-hydroxyaryl ethynyl ketones.*

INTRODUCTION

o-Hydroxyaryl ethynyl ketones have recently attracted much interest as versatile precursors for the synthesis of five and six membered heterocycles.[1-5] We have shown that this type of α,β-acetylenic carbonyl compounds are easily accessible under neutral conditions by the photochemical Fries rearrangement of aryl esters of the corresponding alkynoic acids.[1,6]

In view of these precedents and as a part of our work aimed at the synthesis of flavonoids by application of the photo-Fries transposition, we were interested in the photoreactivity of diaryl esters of acetylenedicarboxylic acid (ADA), in order to explore their potential as new precursors of heterocyclic compounds with structure of chromone or benzocoumaran-3-one, depending on the preferred cyclization mode of the expected o-hydroxyaryl ketones.

Surprisingly, the preparation of diaryl acetylenedicarboxylates is not as obvious task as it could have been initially assumed. In fact, although DMAD is a very important reagent in organic synthesis for cycloadditions and Michael additions, it is noteworthy that literature reports concerning other ADA ester derivatives are much less frequent[7].

In this context, an exhaustive search through the chemical literature reveals that only two reports describe the preparation of aryl esters of ADA. In one of them, a series of 4-alkoxyphenyl esters 1 were obtained by direct reaction of ADA with excess of 4-alkoxyphenols catalyzed by sulfuric acid.[8] Yields of 1 were not given and the formation of other by-products was not mentioned. In the second one, the esterification was carried out in low yield by treatment of acetylenedicarbonyl fluoride with two equivalents of phenol.[9] The use of highly corrosive SF_4 fluorinating agent constitutes one important limitation of this second method. Moreover, the

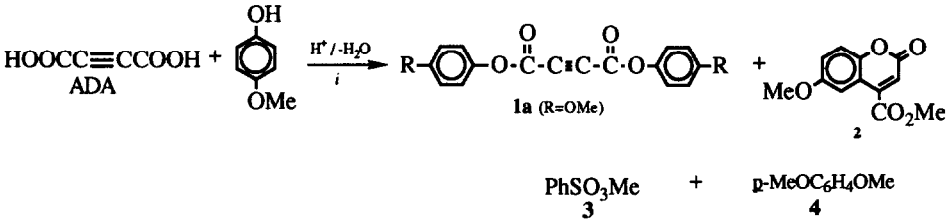
reaction of thionyl chloride with ADA affords the chlorine *syn* addition products to the C≡C triple bond,[10] while the preparation of acetylenedicarbonyl chloride has been more recently reported in the context of the Diels-Alder cycloadditions.[11]

In the present paper, we inform about our results on the esterification of ADA with phenols following three general procedures, and the irradiation of two para substituted aryl esters of ADA 1a,b. We have also observed that the predominant heterocyclization of the photoproducts in the ADA series leads to benzocoumaran-3-ones (5-exo-dig mode), in sharp contrast with the behaviour of β-unsubstituted or alkyl substituted alkynoic acid derivatives, where the 6-endo-dig intramolecular cyclization leading to chromones is the only ring closure observed.

RESULTS AND DISCUSSION

Obtention of diaryl acetylenedicarboxylates 1a,b

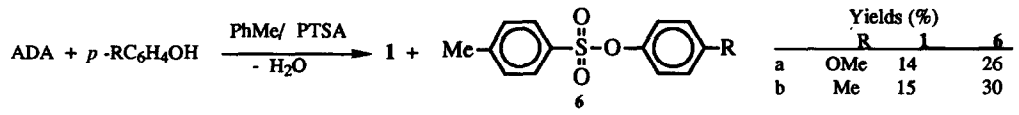
In the first stage of our work, the reaction of ADA with excess of 4-methoxyphenol was carried out in the presence of sulfuric acid under continuous removal of water to shift the esterification equilibrium. These conditions are essentially the same as those previously reported for the preparation of 1a.[8] In our hands, the above treatment led to the expected aryl ester 1a, together with a mixture of the coumarin 2, methyl benzenesulfonate (3) and 1,4-dimethoxybenzene (4).



Scheme 1. Results of the reaction of ADA with 4-methoxyphenol in the presence of sulfuric acid

While the formation of coumarins by reaction of ADA with phenols,[12] and the sulfonation of benzene are well known processes, the less foreseable fact was the presence of methoxy groups in their structures. This can be justified assuming a methyl transfer from the protonated 4-methoxyphenol (5) to the free hydroxy groups.

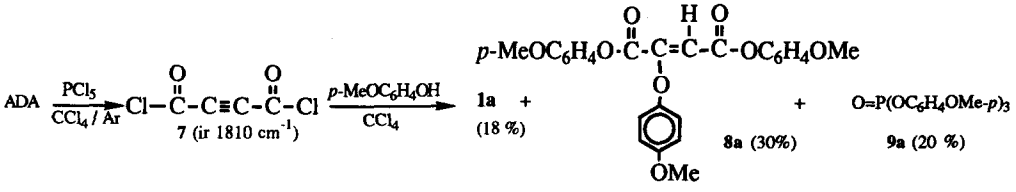
Since the above esterification procedure is a heterogeneous process, it suffers from the disadvantage of the lack of reproducibility. In order to overcome these inconveniences, we repeated the reaction changing sulfuric by 4-toluenesulfonic acid. This modification led to an improved reliability of the process, as well as an appreciable increase on the yield of 1a. Under these conditions, compounds 2-4 were not formed, but the corresponding toluenesulfonate of 4-methoxyphenol (6a) was present as a by-product. A similar product distribution was attained in the preparation of 1b using p-cresol and 4-toluenesulfonic acid as catalyst (Table 1).



		Yields (%)	
	R	1	6
a	OMe	14	26
b	Me	15	30

Table 1.Results of the esterification of ADA catalysed by *p*-toluenesulfonic acid (PTSA)

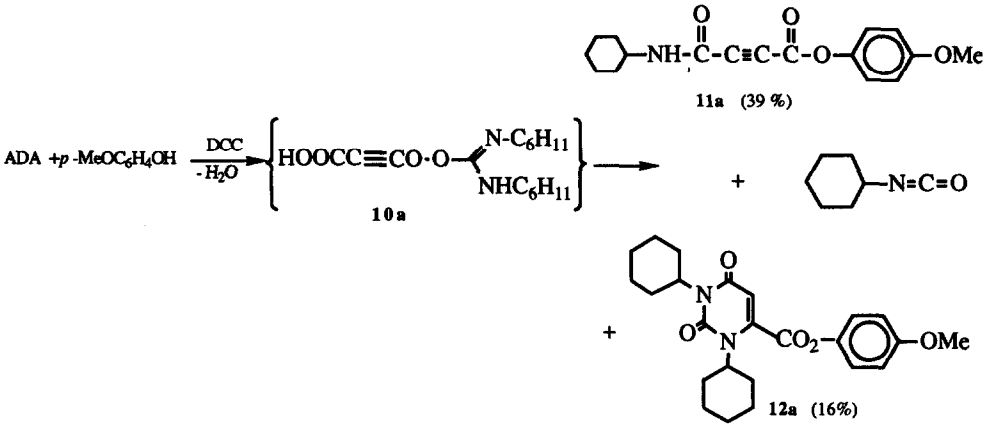
In view of the above results, the preparation of diaryl ester 1a was also attempted through the intermediacy of the acetylenedicarbonyl chloride (7a), generated in situ by stirring at room temperature a suspension of ADA in CCl_4 with PCl_5 under argon stream, following the previously described procedure.[11] The presence of the acyl chloride 7a in the CCl_4 solution was confirmed by observation of a strong absorption band at 1810 cm^{-1} in the ir-spectra. Subsequent addition of 4-methoxyphenol gave rise predominantly to the 4-aryloxyfumarate 8a and the aryl phosphate 9a, together with the expected acetylenedicarboxylate 1a (scheme 2). The formation of these products can be easily understood through well known processes, being worth mentioning that α-phenoxyfumarate has been also obtained, even in higher yields, in the reaction of acetylenedicarbonyl fluoride with phenol.[9] The relative yields of aryloxyfumarates in the acyl halide series, as well as the absence of these compounds when starting from ADA, are in agreement with the predicted enhanced polarity of the carbonyl group, clearly showing that slight modifications of the substituent attached to the C ≡ C triple bond may result in a remarkable difference on the behaviour of this function towards nucleophilic addition (Scheme 2).



Scheme 2. Results of the esterification of ADA through the intermediacy of the corresponding dichloride

The esterification of ADA with 4-methoxyphenol was finally attempted using *N,N'*-dicyclohexylcarbodiimide as condensing agent and 4-(*N,N*-dimethyl)aminopyridine (DMAP) as catalyst. The diester 1a could not be detected under these reaction conditions, but instead the aryl 3-(*N*-cyclohexylaminocarbonyl)propynoate 11a and the substituted uracil 12a were isolated from the reaction mixture (Scheme 3). As far as we are aware, compound 11a constitutes the first example of an asymmetric ester amide derivative of ADA.

A reasonable explanation to account for these results would imply activation of ADA through the key intermediate 10a.[13] On the other hand we were able to obtain experimental evidence by GC-MS and GC-FTIR for the formation of cyclohexylisocyanate.[14]



Scheme 3. Attempted esterification of ADA using *N,N* -dicyclohexylcarbodiimide (DCC) as condensing agent.

Photolysis of diaryl acetylenedicarboxylates 1a,b

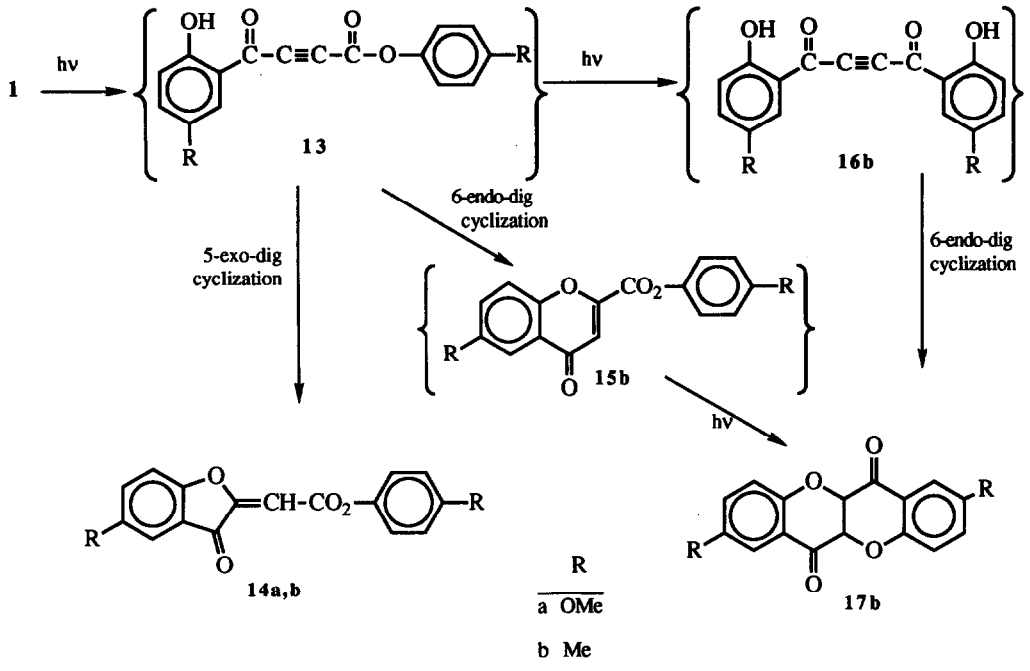
Irradiation of diaryl esters 1a,b in benzene solutions (2.10^{-3} M) for a short time resulted in the complete disappearance of the starting compound and formation of the benzocoumarones 14a,b, together with substantial amounts of the corresponding phenols and unidentified polymeric material. In the case of methyl substituted ester 1b, the condensed polycyclic 4-chromanone 17b was also isolated.

Taking into account the photochemical reactivity pattern of aryl alkynoates and related esters of α,β-unsaturated carboxylic acids which undergo a photo-Fries rearrangement upon irradiation,[1,6,15] the formation of benzocoumarones 14 can be justified assuming that the initial 'normal' photo-Fries products 13a,b undergo a spontaneous intramolecular ring closure under our reaction conditions (Scheme 4).

Likewise, a double photo-Fries rearrangement of the two aryl ester moieties of 1b, coupled with intramolecular cyclizations can easily explain the formation of the chromanone derivative 17b. However, inspection of the product distribution does not allow at the present to assess the exact sequential order of these transposition-cyclization processes and two possible compounds with structure of chromone 15b or diketone 16b can be invoked as intermediates.

According to Scheme 4, the intramolecular nucleophilic attack of the phenolic OH group to the C ≡ C triple bond for the α,β-acetylenic ketones 13 takes place predominantly (or even exclusively if the chromanone 17b arises from the diketone 16b) following a 5-exo-dig cyclization mode.[16]

It is known that o-hydroxyaryl ethynyl or propynyl ketones undergo a 6-endo-dig ring closure,[6] while for aryl phenylethynyl ketones both types of attacks (5-exo-dig and 6-endo-dig) are competitive, the preferred mode depending basically on the protic or aprotic nature of the medium employed.[1] Therefore, our present finding contributes to further complete the picture of intramolecular attacks to the C ≡ C triple bond in aryl ethynyl ketones, showing that the ability of the group attached to the β position of the acetylenic moiety to stabilize an incipient negative charge plays an important role in the course of the reaction.



Scheme 4.Photolysis of aryl acetylenedicarboxylates **1a,b**

ACKNOWLEDGEMENTS

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EXPERIMENTAL

Melting points are uncorrected and were measured using a Büchi 510 apparatus. Ir spectra were obtained in CCl_4 solutions or KBr disks with a Perkin-Elmer 851 spectrophotometer; wavenumber absorptions (cm^{-1}) are given only for the most significant bands. ^{1}H-nmr spectra were recorded in CCl_4 or $CDCl_3$ with a 60 MHz Varian 360 EM or a 300 MHz Varian mod. Geminis (15b); ^{13}C-nmr were run in $CDCl_3$ solutions using a Bruker WP 80 SY spectrometer; chemical shifts are reported as δ values (ppm) using TMS as internal standard; coupling constants are given in Hz. Mass spectra were determined with a Hewlett-Packard 5988 A spectrometer; m/z ratio and their relative abundances in percentages (in brackets) are given only for the main peaks. GC-FTIR spectrum of the reaction mixture of ADA with 4-methoxyphenol using N,N'-dicyclohexylcarbodiimide as condensing agent was carried out with a Hewlett-Packard 5890 GC coupled with a Hewlett-Packard 5965 A FTIR detector provided with a 25 m capillary column of crosslinked 5% phenylmethyl silicone. Elemental analyses were performed at the Instituto de Química Bio-Orgánica of C.S.I.C. in Barcelona. Isolation and purification of the reaction mixtures were done by flash column chromatography on silica gel Merck 60, 70-230 mesh using mixtures of hexane/ether as eluent.

Reaction of acetylenedicarboxylic acid with 4-methoxyphenol catalyzed by sulfuric acid.

To a solution of 4.50 g (36.30 mmol) of 4-methoxyphenol in benzene (100 ml) was added sulfuric acid (0.50 ml) and then 1.00 g (8.8 mmol) of acetylenedicarboxylic acid. The mixture was heated at reflux temperature for 24 h using a Dean-Stark equipment. After this time, the suspension was neutralized with an aqueous solution (10 % w/w) of $NaHCO_3$, and the aqueous layer thoroughly extracted with ethyl ether. The combined organic solutions were dried over anhydrous Na_2SO_4, the solvents removed under vacuum, and the residue submitted to column chromatography. The following products were isolated:

Methyl benzenesulfonate (3, 475 mg, 7%).

Bis-4-methoxyphenyl acetylenedicarboxylate (1a, 227 mg, 8%). m.p. 146-147°C (lit.[8], 148-150°C); ir (CCl_4) 1760 (C=0); ^{1}H-nmr ($CDCl_3$) 7.10-6.79 (AA'BB', J=8, 8H, Ar-H), 3.83 (s, 3H, OCH_3).

1,4-Dimethoxybenzene (4, 50 mg, 12%).

Methyl 6-methoxycoumarin-4-carboxylate (2, 425 mg, 5%); ir (CCl_4) 1725 (C=O); ^{1}H-nmr ($CDCl_3$): 7.88-7.12 (m, 3H, ArH), 6.90 (s, 1H, H at C-3), 4.10 (s, 3H, CO_2-CH_3), 3.84 (s, 3H, $ArOCH_3$); ^{13}C-nmr ($CDCl_3$): 164.2, 159.9, 156.4, 148.7, 141.7, 120.3, 119.99, 118.0, 109.3, 55.8, 52.9; ms: 234 (M^+, 80), 206 (43), 175 (100), 147 (41).

Reaction of acetylenedicarboxylic acid with phenols catalyzed by p-toluenesulfonic acid.

To 1.00 g (8.80 mmol) of acetylenedicarboxylic acid dissolved in toluene (100 ml), the corresponding phenol (36.30 mmol) and 100 mg (0.53 mmol) of 4-toluenesulfonic acid were added. The mixture was heated at reflux temperature using a Dean-Stark apparatus during 24 h. The raw material was washed with a solution of $NaHCO_3$ (5 %) and dried over anhydrous Na_2SO_4. After elimination of the solvent the residue was purified by column chromatography.

Reaction with 4-methoxyphenol. The following products were isolated:

4-Methoxyphenyl p-toluenesulfonate (6a, 43 mg, 26 %); ir (CCl_4): 1400 (S=O), 1170 (S-O); ^{1}H-nmr (CCl_4): 7.67 (d, J=7, 2H, aromatic H ortho to SO_2), 7.29 (d, J=7, 2H, aromatic H meta to SO_2), 6.81 (AA'BB', J=7, 4H, CH_3O-C_6H_4-O), 3.78 (s, 3H, OCH_3), 2.48 (s, 3H, Ar-CH_3).

Bis-4-methoxyphenyl acetylenedicarboxylate (1a, 391 mg, 14 %).

Reaction with 4-methylphenol. The following products were isolated:

4-Methylphenyl p-toluenesulfonate (6b, 45 mg, 30 %), ir (CCl_4): 1380 (S=O), 1175 (S-O); ^{1}H-nmr: (CCl_4) 7.65 (d, J=7, 2H, aromatic H ortho to SO_2), 7.24 (d, J=7, 2H, aromatic H meta to SO_2), 6.69 (AA'BB', J=7, 4H, CH_3-C_6H_4-O), 2.47+2.30 (s+s, 6H, $2CH_3$).

Bis-4-methylphenyl acetylenedicarboxylate (1b, 388 mg, 15 %), m.p. 135-136°C; analysis: C 73.41 H 4.58 % (Calcd. for $C_{18}H_{14}O_4$: C 73.46 H 4.80 %); ir: 1755 (C=O); ^{1}H-nmr (CCl_4): 7.39-6.97 (AA'-BB', 8H, Ar-H), 2.38 (s, 6H, $2CH_3$).

Reaction of acetylenedicarboxylic acid with PCl_5 and ulterior addition of 4-methoxyphenol.

A suspension of acetylenedicarboxylic acid (1.14 g, 10 mmol) and PCl_5 (4.16 g, 20 mmol) in CCl_4, was stirred at room temperature under Ar stream during 4 h. After this time the ir spectrum of the liquid phase showed an intense absorption at 1810 cm^{-1}. The solution was treated with 4-methoxyphenol (2.48 g, 20 mmol) and catalytic amounts of DMAP, with stirring at room temperature for 1 h. After this time, the solvent was

removed under vacuum and the residue purified by column chromatography using hexane as eluent.

The following products were isolated:

Bis-4-methoxyphenyl acetylenedicarboxylate (1a, 587 mg, 18 %).

Bis-4-methoxyphenyl 4-methoxyphenoxyfumarate (8a, 1.35 g, 30 %). Mp 103-105°C; analysis: C 66.41, H 4.67 % (Calcd. for $C_{25}H_{22}O_8$: C 66.81 , H 4.67 %); ir (CCl_4): 1760 (C=O), 1730 (C=O); ^{1}H-nmr ($CDCl_3$): 7.57 (s, 1H, C=C<u>H</u>), 7.36-6.70 (m, 12H, Ar-H), 3.81 (s, 9H, 3xOC<u>H</u>$_3$).

Tris-(4-methoxyphenyl) phosphate (1.66 g, 20 %); analysis: C 60.21, H 5.32 % (Calcd. for $C_{21}H_{21}O_7P$: C 60.59, H 5.08 %); ir (CCl_4): 1190 (PO), 1040 (PO); ^{1}H-nmr ($CDCl_3$): 7.22-6.71 (AA'-BB', 12H, Ar-<u>H</u>), 3.79 (s, 9H, 3xOC<u>H</u>$_3$); ^{13}C-nmr ($CDCl_3$): 157.1 ($J_{C\text{-}Ppara}$=1.4), 144.1 ($J_{C\text{-}Pipso}$=7.6), 120.9 ($J_{C\text{-}Portho}$=4.8), 114.7, 55.5; ms :416 (M^+, 23), 293 (1), 230 (5), 215 (3), 208 (2), 170 (5), 123 (100).

Reaction of acetylenedicarboxylic acid with 4-methoxyphenol using N,N'-dicyclohexylcarbodiimide as condensing agent.

A solution of DCC (4.12 g, 20 mmol) in CH_2Cl_2 (20 ml) was added slowly to a mixture of acetylenedicarboxylic acid (1.14 g, 10 mmol), 4 methoxyphenol (2.48 g, 20 mmol) and DMAP (294 mg) in CH_2Cl_2 (50 ml). . The mixture was stirred at room temperature for 15 min, then filtered to remove the precipitated N,N'-dicyclohexylurea, concentrated in vacuo and purified by chromatography. The following products were isolated:

1,3-Dicyclohexyl-6-(4-methoxyphenoxycarbonyl)uracil (12a, 682 mg, 16 %); analysis: C 67.80, H 7.11, N 6.23 % (Calcd. for $C_{24}H_{30}N_2O_5$: C 67.58, H 7.09, N 6.57 %); ir (CCl_4): 1765 (C=O), 1730 (C=O), 1640 (C=O); ^{1}H-nmr (CCl_4): 7.38-6.63 (AA'BB', 4H, Ar-<u>H</u>), 5.66 (s, 1H, =C<u>H</u>), 3.81 (s, 3H, OC<u>H</u>$_3$), 2.38-0.82 (m, 22H, 2xC_6H_{11}); ^{13}C-nmr ($CDCl_3$): 197.5, 164.5, 160.5, 157.4, 144.2, 135.2, 122.2, 114.5, 100.5, 55.5, 53.7, 51.9, 29.4, 29.2, 25.9, 25.7, 25.0, 24.9; ms: 426 (M^+, 1), 303 (100), 221 (41), 139 (75), 124 (15).

4-Methoxyphenyl 3-(N-cyclohexylaminocarbonyl)propynoate (11a, 1.174 g, 39 %). Mp: 152-154°C; analysis: C 67.44, H 6.77, N 4.95 % (Calcd. for $C_{17}H_{19}NO_4$: C 67.76, H 6.35, N 4.65 %); ir (CCl_4): 3300 (N-H), 2140 (C≡C), 1780 (C=O), 1730 (C=O), 1645; ^{1}H-nmr (CCl_4): 7.28-6.75 (m, 4H, Ar-<u>H</u>), 6.15 (s, 1H, N<u>H</u>), 3.84 (s, 3H, OC<u>H</u>$_3$), 2.46-0.91 (m, 11H, C_6H_{11}).

Photolysis of Bis-4-methoxyphenyl acetylenedicarboxylate 1a

A solution of the aryl ester 1a (300 mg) in benzene (450 ml) was irradiated for 15 min using a quartz immersion well photoreactor provided with a 125 W medium pressure mercury lamp. After this time, the reaction mixture was concentrated and submitted to column chromatography using hexane-dichloromethane as eluent. The following products were isolated:

4-Methoxyphenol (44 mg, 24 %).

4-Methoxyphenyl 5-methoxy-3-oxo-2(3H)-benzofuranylideneacetate (14a, 69 mg, 23 %). Mp 175-176°C; analysis: C 65.92, H 4.22 % (Calcd. for $C_{18}H_{14}O_6$: C 66.26, H 4.32 %); ir (CCl_4): 1745 (C=O), 1715 (C=O); ^{1}H-nmr ($CDCl_3$): 7.36-6.74 (m, 7H, Ar-<u>H</u>), 6.29 (s, 1H, =C<u>H</u>), 3.83+3.82 (s+s, 6H, 2xOC<u>H</u>$_3$).

Photolysis of Bis-4-methylphenyl acetylenedicarboxylate 1b

Following the irradiation procedure described for 1a, the photolysis of the diester 1b (250 mg, 0.8 mmol) gave:

4-Methylphenol (40 mg, 22 %).

4-Methylphenyl 5-metyl-3-oxo-2(3H)-benzofuranylideneacetate (14b, 60 mg, 24 %). Mp 110-112°C; analysis: C 73.72 H 4.58 % (Calcd. for $C_{18}H_{14}O_4$: C 73.46, H 4.79 %); ir (CCl_4): 1730 (C=O), 1705 (C=O); ^{1}H-nmr ($CDCl_3$) 7.69-7.08 (m, 7H, Ar-H), 6.20 (s, 1H, =CH), 2.40 (s, 3H, CH_3), 2.36 (s, 3H, CH_3); ms 294 (M^+, 9), 187 (100), 108 (5).

Bis(methylbenzo)[(4,3-c),(4,3-h)]-2,7-dioxa[4.4.0]bicyclodecane-5,10-dione (17b, 30 mg, 12 %); analysis: C 73.54, H 4.96 % (Calcd. for $C_{18}H_{14}O_4$: C 73.46, H 4.79 %); ir (CCl_4): 1710 (CO); ^{1}H-nmr($CDCl_3$): 7.52-6.83 (m, 6H, ArH), 5.14+5.11 (s+s, 2H, 2xCH), 2.36+2.35 (s+s, 6H, 2xCH_3-Ar); ms: 294 (M^+, 60), 293 (38), 265 (55), 134 (100).

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