The conversion efficiency for the photoelectrolytic mode was larger than for the photovoltaic one. We attribute this difference to the fact that the Pt counter-electrode has a large over-potential relative to the redox couple (OH^-/O_2) level.

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ARTIGO

SYNTHESIS OF WYERONE BENZENE ANALOGUE, ITS EPOXIDE DERIVATIVE AND OTHERS α-ALKYNYLCARBONYL COMPOUNDS

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ABSTRACT

Methyl 3-[4-(hept-4*Z*-en-2-yn-1-one)-phenyl]-prop-2*E*-enoate, its epoxide derivative and others α-alkynylcarbonyl compounds were prepared through Grignard's reaction.

INTRODUCTION

Wyerone (*1*) and wyerone-epoxide (*2*) are phytoalexins of plants belonging to Papilionaceae family[1,2,3]. Their tiophenic structural analogues were synthesized by Thaller

et al and presented identical fungitoxic properties[4].

Now considering the recognized antibiotic activity of α-alkynylcarbonyl compounds[5], and hoping to obtain structurally stable compounds, we synthesized the benzene analogues of these phytoalexins, basides some others α-alkynylcarbonyl derivatives as model compounds.

RESULTS AND DISCUTIONS

Aiming the improvement of reactional conditions leading to the synthesis of wyerone benzene analogue (*3*) and its epoxide derivative (*4*), we prepared a mixture of *Z* and *E*-hex-3-en-1-yne isomers followed by their Grignard salts, in accordance with the literature[4,6], which then were condensed with various aromatic aldehydes (Table 1).

During the preparation of the tiophenic analogues, when doing Grignard's reaction, Thaller et al used the hex-3*Z*-en-1-yne isomer, previously separated from *Z* and *E* diastereomers mixture. Due to the instability of these precursors, volatility and a narrow difference between their boiling points, this method seemed unappropriate to us. Alternatively, terminal acetylene silylation increasing the range between boiling points and structural stability[7] could be a plausible method.

In our case however, Grignard's reaction followed by hydroxy group oxidation, were both performed with the isomers mixture, that only then was separated into their *Z* and *E* diastereomers. This separation was performed with an excellent result through thin layer chromatography (tlc) continuously eluted, or alternatively through chromatography radially accelerated by centrifugation[8].

Oxidation of alcohols to their corresponding ketones with both manganese dioxide (MnO_2) and pyridinium chlorochromate (*PCC*) was equally efficient. In fact, simply leaving these alcohols under contact with air, for a long time, always resulted in the expected ketones.

On the other hand, the p-formylcinnamic acid (*6*) was obtained from commercial terephtalic acid (*5*) in four steps according to the reaction pathway showed bellow. All steps were slightly modified as compared to usual techniques.

Pathway for the p-formylcinnamic acid obtainment (LAH = $LiAlH_4$).

The main products ^1H N.M.R. data are shown in table 2.

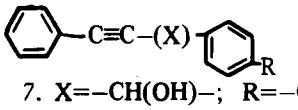
Table 1. Grignard's reaction and subsequent oxidation products.

Reagentes		Alcohol (%)	Ketone (%)	Epoxide (%)
Ph–C≡C–MgBr	4–OCH_3–*Ph*–CHO	*7* (89)	*8* (100)	–
Ph–C≡C–MgBr	4–CHO–Cinnamic Ac.	*9* (51)	*10* (50)	–
C_2H_5–CH=CH–C≡C–MgBr	4–OCH_3–*Ph*–CHO	*11*⁺ (89)	*12*⁺ (93)	*16* (51)
C_2H_5–CH=CH–C≡C–MgBr	furfural	*14*⁺ (87)	*15*⁺ (89)	*17* (43)
C_2H_5–CH=CH–C≡C–MgBr	4–CHO–Cinnamic Ac.	*13**⁺ (83)	*3*⁺ (91)	*4* (44)

* Non-isolated and immediately estherified (esther percentage).

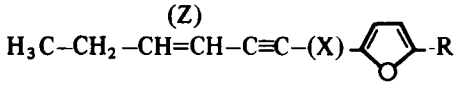
⁺ Diastereomers mixture (*Z* and *E*).

General structure:



7. X=–CH(OH)–; R=–OCH_3
8. X=:CO–; R=–OCH_3
9. X=-CH(OH)–; (E)
9. X=–CH(OH)–; R=–CH=CH–CO_2H
(E)
10. X=–CO–; R=–CH=CH–CO_2H

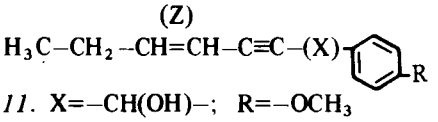
(Z)



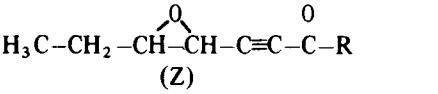
(E)
1. X=–CO–; R=–CH=CH–CO_2CH_3

14. X=–CH(OH)–; R=H
15. X=–CO–; R=H

(Z)

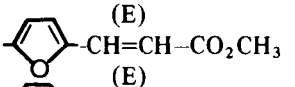


11. X=–CH(OH)–; R=–OCH_3
12. X=–CO–; R=–OCH_3
(E)
13. X=:CH(OH); R=–CH=CH–CO_2CH_3
(E)
3. X=–CO–; R=–CH=CH–CO_2CH_3

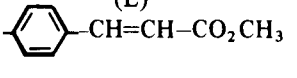


(Z)

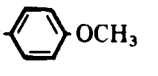
(E)



2. R=–CH=CH–CO_2CH_3
(E)



4. R=–CH=CH–CO_2CH_3



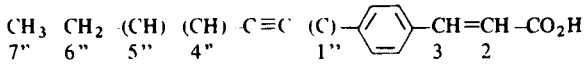
16. R=–OCH_3

17. R=

Table 2. ^{1}H-NMR data of compounds *13*–(4"*Z*), *13* (4"*E*), *3* (4"*Z*), *3* (4"*E*) and *4* (*E*-epoxide); δ scale (at 100 MHz, solvent $CDCl_3$).

Compound Proton	*13*–(4"*Z*)	*13*–(4"*E*)	*3*-(4"*Z*)	*3*–(4"*E*)	*4*–(*E*-epoxide)
H-7"	1.01 *t* (7.5)	1.01 *t* (7.5)	1.15 *t* (7.4)	1.12 *t* (7.4)	1.17 *t* (7.0)
H-6"	2.2 *m*	2.3 *m*	2.53 *m*	2.3 *m*	1.65 *m*
H-5"	5.94 *dt* (5.4=10.5 & 5.6=1.0)	6.20 *dt* (5.4=16.0 & 5.6=6.4)	6.34 *dt* (5.4=10.6 & 5.6=7.4)	6.77 *dt* (5.4=16.0 & 5.6=6.0)	3.28 *dt* (5.4=3.6 & 5.6=6.0)
H-4"	5.47 *dt* (4.5=10.5 & 4.6=1.5)	5.49 *dt* (4.5=16.0 & 4.6=1.5)	5.70 *dt* (4.5=10.6 & 4.6=1.2)	5.74 *dt* (4.5=16.0 & 4.6=1.0)	3.60 *dt* (4.5=3.6 & 4.6=1.0)
H 1"	5.47 *s*	5.47 *s*	–	–	–
H 2'& 6'	7.48 *br*	7.48 *br*	8.13 *d* (8.0)	8.11 *d* (8.5)	8.12 *d* (9.0)
H-3'& 5'	7.48 *br*	7.48 *br*	7.68 *d* (8.0)	7.61 *d* (8.5)	7.47 *d* (9.0)
H-3	7.66 *d* (16.0)	7.66 *d* (16.0)	7.64 *d* (16.0)	7.68 *d* (16.4)	7.68 *d* (17.0)
H-2	6.32 *d* (16.0)	6.32 *d* (16.0)	6.48 *d* (16.0)	6.47 *d* (16.4)	6.48 *d* (17.0)
OCH_3	3.76 *s*	3.76 *s*	3.78 *s*	3.78 *s*	3.80 *s*
OH-1	3.40 *s*	3.40 *s*	–	–	–
H-7"	1.01 *t* (7.5)	1.01 *t* (7.5)	1.15 *t* (7.4)	1.12 *t* (7.4)	1.17 *t* (7.0)
H-6"	2.2 *m*	2.3 *m*	2.53 *m*	2.3 *m*	1.65 *m*
H 5"	5.94 *dt* (5.4=10.5 & 5.6=7.0)	6.20 *dt* (5.4=16.0 & 5.6=6.4)	6.34 *dt* (5.4=10.6 & 5.6=7.4)	6.77 *dt* (5.4=16.0 & 5.6=6.0)	3.28 *dt* (5.4=3.6 & 5.6=6.0)
H-4"	5.47 *dt* (4.5=10.5 & 4.6=1.5)	5.49 *dt* (4.5=16.0 & 4.6=1.5)	5.70 *dt* (4.5=10.6 & 4.6=1.2)	5.74 *dt* (4.5=16.0 & 4.6=1.0)	3.60 *dt* (4.5=3.6 & 4.6=1.0)
H 1"	5.47 *s*	5.47 *s*	–	–	–
H-2'& 6'	7.48 *br*	7.48 *br*	8.13 *d* (8.0)	8.11 *d* (8.5)	8.12 *d* (9.0)
H-3'& 5'	7.48 *br*	7.48 *br*	7.68 *d* (8.0)	7.61 *d* (8.5)	7.47 *d* (9.0)
H-3	7.66 *d* (16.0)	7.66 *d* (16.0)	7.64 *d* (16.0)	7.68 *d* (16.4)	7.68 *d* (17.0)
H-2	6.32 *d* (16.0)	6.32 *d* (16.0)	6.48 *d* (16.0)	6.47 *d* (16.4)	6.48 *d* (17.0)
OCH_3	3.76 *s*	3.76 *s*	3.78 *s*	3.78 *s*	3.80 *s*
OH-1	3.40 *s*	3.40 *s*	–	–	–

Signals are designed as follows: *s*, singlet; *d*, doublet; *dt*, double triplet; *t*, triplet; *m*, multiplet; *br*, unresolved or broad. Figures in parenthesis are the number of carbon to which proton are bonded and coupling constant in Hz, respectively; internal reference: TMS.



We must finally emphasize that the main products as well as the obtained and described models in this work are are unpublished, except for that shown by structure *8*[9], and deserve special attention. Firstly because of the extraordinary structural stabilities presented by wyerone benzene analogue and its epoxide derivative. Secondly because all them are alkynylketones which might probably present some antibiotic properties, and were easily prepared through simple and classical methods.

EXPERIMENTAL

a) General methods: UV were runned in Et_2O; I.R. in $CHCl_3$ or KBr pellets; column chromatography and tlc were performed with silicagel G and PF_{254} respectively; mps are uncorrected; MS at 70 e V.

b) Typical procedure:

Methyl (±) 3-[4-(hept-4-en-2-yn-1-ol)-phenyl]-prop-2*E*-enoate (*13*) – To a mixture of *Z* and *E*-hex-3-en-1-ynylmagnesium bromide (392 mg) prepared according to the literature[4], in dry tetrahydrofuran (THF) (10 ml) at 0°C, p-formylcinnamic acid (376 mg) was added in a single portion. The mixture was allowed to warm up to room temperature (r.t.) and the reaction followed by t.l.c. (completed in 35 min.). The crude product was poured on cold aqueous HCl (5%, 5 ml), extracted with ether and immediately estherified with diazomethane in excess, at r.t. After removing solvent, the residue was chromatographed on silicagel column affording a colourless oil, 83% (479 mg). Spectral data: IR (ν_{max}^{film} cm^{-1}) 3400 br, 2950, 2210, 1700, 1630, 1430, 1330, 1280, 1200; MS m/z

(relative intensity) 270 M^+ (100), 255 (51), 239 (28), 241 (84), 211 (19), 209 (32), 189 (39), 107 (62), 105 (19), 79 (21). ^{1}H-NMR – Table 2.

(±) 3-Phenyl-1-(p-methoxyphenyl)-prop-2-yn-1-ol (*7*) – Prepared as described for preparation of the alcohol *13*, to give compound *7*, as a colourless oil, slightly unstable, 89%. Spectral data: ^{1}H-NMR (at 60 Mz, CCl_4) 7.60 d (J = 8.0 Hz, 2 H), 7.0 br (5 H), 6.93 d (J = 8.0 Hz, 2 H), 5.63 s 91 H), 3.80 s (3 H), 2.95 br (1 H).

(±) Hept-1-(p-methoxyphenyl)-4 E/Z-en-2-yn-1-ol (*11*) – Prepared as described for preparation of the alcohol *13*, to give compound *11*, as a colourless oil, very unstable, 89%. Spectral data: IR [ν_{max}^{film} (cm^{-1})] 3400 br, 2980, 2950, 2220, 1620, 1590, 1520, 1310, 1260, 1180, 1110, 1000, 970, 840, 810; MS m/z (%) 216 M^+ (58), 201 (24), 187 (39), 135 (29), 108 (100), 79 (14), 77 (39); ^{1}H-NMR of *Z* compound (60 Mz, CCl_4): 7.37 d (J = 9.0, 2 H), 6.75 d (J = 9.0, 2 H), 5.97 dt ($J_{5,4}$ = 10.0 Hz & $J_{5,6}$ = 7.0 Hz, 1 H), 5.50 d ($J_{4,5}$ = 10.0 Hz, 1 H), 5.4 br (1 H), 3.77 s (1 H), 2.20 m (2 H), 1.03 t (J = 7.5 Hz, 3 H).

(±) Hept-1-(2-furyl)-4 E/Z-en-2-yn-1-ol (*14*) – Prepared as described for preparation of the alcohols above, to give compound *14*, is a colourless oil, unstable. Spectral data: IR [ν_{max}^{film} (cm^{-1})]: 3350 br, 2980, 2920, 2220, 1500, 1460, 1300, 1140, 1000 br, 740; MS m/z (%) 176 M^+ (50), 161 (20), 159 (26), 147 (100), 107 (19), 105 (41), 95 (70), 79 (33), 77 (67); ^{1}H-NMR of *Z* compound (60 Mz, CCl_4) 7.33 br (1 H), 6.30 m (2 H), 5.93 dt ($J_{4,5}$ = 10.4 Hz & $J_{4,6}$ = 7.0 Hz, 1 H), 5.5 br (2 H), 3.58 br (1 H), 2.20 m (2 H), 1.02 t (J = 7.2 Hz, 3 H).

Methyl 3-[-4-(hept-4*Z*-en-2-yn-1-one)-phenyl]-prop-2*E*-enoate (*3*) – To a mixture *Z* and *E*-"esther" *13* 9134 mg) in CCl_4 (10 ml) at 0°C, under stirring, MnO_2 powder (620 mg) was added in a single portion. The mixture was allowed to warm up to r.t. and followed by t.l.c. until completion (ca. 20 min). The product was filtered, the solvent evaporated at r.t. and the residue chromatographed on "Chromatotron" (elution in hexane-methanol 3%) affording the "ketone" *3Z*, 47% (56 mg) and its *E*-isomer, 43% (52 mg), mps 71-73° and 61-63°C (petrol) respectively. Spectral data (*Z*-isomer): IR (ν_{max}^{KBr} cm^{-1}) 2980, 2190, 1715, 1640, 1600, 1270, 1210, 1180, 990, 930; UV [$\lambda_{max}^{Et_2O}$ nm (ϵ)] 311 (45120); MS m/z (%) 268 M^+ (100), 234 (13), 209 (8), 207 (10), 189 (35), 107 (57), 105 (23), 79 (14); ^{1}H-NMR – Table 2.

Methyl, 3-[4-(3-phenyl-2-yn-1-one)-1-phenyl]-prop-2*E*-enoate (*10*) – Prepared as described for the preparation of the ketone *3*, to give compound *10* as an oil very unstable. IR da ($\nu_{max}^{CCl_4}$ cm^{-1}): 2920, 2850, 2195, 1730, 1635, 1540, 1430, 1320, 1310, 1275, 1250, 1200, 1165, 1025, 1010, 990, 980.

Hept-1-(p-methoxyphenyl)-4 *E/Z*-en-2-yn-1-one (*12*) – Prepared as described for the preparation of ketones above, to give an oil unstable. Spectral data: IR (ν_{max}^{film} cm^{-1}) 2960, 2930, 2180, 1635, 1600, 1570, 1510, 1460, 1420, 1320, 1300, 1260, 1170, 1030, 960, 930, 870, 840, 760, 690; MS m/z (%) from *E* compound – 214 M^+ (100), 185 (9), 135 (40), 107 (17), 105 (13), 77 (46); ^{1}H-NMR of *E* compound (60 MHz, CCl_4) 8.05 d (J = 9.0 Hz, 2 H), 6.90 d (J = 9.0 Hz, 2 H), 6.61 dt ($J_{5,4}$ = 16.0 & $J_{5,6}$ = 6.0 Hz, 1 H), 5.70 dt ($J_{4,5}$ = 16.0 Hz & $J_{4,6}$ = 1.2 Hz, 1 H), 3.90 s (3 H), 2.32 m (2 H), 1.15 t (J = 7.6, 3 H).

1-(2-Furyl)-hept-4 *Z/E*-en-2-yn-1-one (*15*) – Prepared as described for preparation of ketones above, to give a colourless oil unstable. Spectral data of *Z* isomer: IR (ν_{max}^{film} cm^{-1}) 3120, 2960, 2180, 1625, 1600, 1560, 1460, 1390, 1300, 1165, 1010, 945, 840; MS m/z (%) 174 M^+ (91), 145 (15), 107 (15), 95 (100), 79 (11), 77 (70), 59 (20); ^{1}H-NMR (60 MHz, CCl_4) 7.68 d (J = 2.0 Hz, 1 H), 7.27 d ($J_{3',4'}$ = 3.5 Hz, 1 H), 6.33 dt ($J_{5,4}$ = 11.0 Hz & $J_{5,6}$ = 7.5 Hz, 1 H), 5.65 dt ($J_{4,5}$ = 11.0 Hz & $J_{4,6}$ = 1.0 Hz, 1 H), 5.57 dd ($J_{4',3'}$ = 3.5 Hz & $J_{4',5'}$ = 2.0 Hz, 1 H), 2.50 m (2 H), 1.13 t (J = 7.5 Hz, 3 H).

Methyl (±) 3-[4-(hept-4,5*Z*-epoxide-2-yn-1-one)-phenyl]-prop-2*E*-enoate (*4*) – "Ketone" 3*Z* (32 mg) and *m*-chloroperbenzoic acid (22 mg) were suspended on CCl_4 (2 ml) and heated to 50°C, under stirring. The reaction was followed by t.l.c. until completion (ca. 8 hr). The mixture was then poured on cold aqueous Na_2CO_3 (5%, 5 ml) and the organic layer extracted with ether. After solvent evaporation, the residue was chromatographed on silicagel (p.l.c.; PF_{254}; elution petrol-ether 4:1) affording "epoxide *4*" colourless cristals, 44% (15 mg), m.p. 81-83°C (CCl_4). Spectral data: IR (ν_{max}^{KBr} cm^{-1}) 2950, 2200, 1725, 1645, 1600, 1430, 1410, 1310, 1265, 1200, 1170, 980, 840, 670; UV [$\lambda_{max}^{Et_2O}$ nm (ϵ) 305 (45021); MS m/z (%) 284 M^+ (77), 255 (62), 226 (64), 198 (100), 189 (45); ^{1}H-NMR – Table 2.

(±) Hept-1-(p-methoxyphenyl)-4,5 *Z* -epoxy-2-yn-1-one (*16*) – Prepared as described for preparation of the epoxide *4*, to give a colourless oil. Spectral data: IR (ν_{max}^{film} cm^{-1}) 2960-2920, 2200, 1645, 1595, 1270, 1255, 1160, 1030, 860, 840; MS m/z (%) 230 M^+ (32), 201 (23), 172 (25), 144 (1000, 135 (20), 119 (16), 117 (16), 77 (14); ^{1}H-NMR (100 MHz, CCl_4) 8.25 d (J = 9.3 Hz, 2 H), 7.10 d (J = 9.3 Hz, 2 H), 3.97 s (3 H), 3.65 d ($J_{4,5}$ = 4.0 Hz, 1 H), 3.60 dt ($J_{5,4}$ = 4.0 Hz & $J_{5,6}$ = 6.5 Hz, 1 H), 1.80 m (2 H), 1.12 t (J = 7.4 Hz, 3 H).

(±) 1-(2-Furyl)-hept-4,5 *Z*-epoxy-2-yn-1-one (*17*) – Prepared as described for preparation of the epoxides above, to give a colourless oil, slightly unstable. Spectral data: IR (ν_{max}^{film} cm^{-1}) 3220, 3060, 3020, 2960, 2940,

2310, 1810, 1680, 1610, 1500, 1465, 1440, 1350, 1260, 1220, 1150, 1060, 990, 935, 925, 810; MS m/z (%) 190 M^+ (30), 161 (67), 132 (80), 105 (11), 95 (100), 77 (29), 75 (26), 72 (24); partial ^{1}H-NMR data át 60 MHz (CCl_4) 3.50 d ($J_{4,5}$ = 4.0 Hz, 1 H), 3.00 dt ($J_{5,4}$ = 4.0 Hz & $J_{5,6}$ = 6.0 Hz, 1 H).

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ARTIGO

HETEROCICLOS CONDENSADOS – SÍNTESE PASSO A PASSO

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ABSTRACT

A synthetic route to prepare heterocyclic systems, such as, thieno[3,2-*e*]pyrazolo[4,3-*c*]pyridine from thiofene and its reaction with 1,3-dicarbonileted compounds to yield, a new class of heterocyclic, thieno[3'',2'':5',6']pyrido[3'4':4,3]pyrazolo[1,5-*a*]pyrimidine are discribed.

Elemental analyses and the spectra (I.R., N.M.R. and Mass) were consistent with the expected structures.

1. INTRODUÇÃO

Existe uma grande variedade de substâncias orgânicas que possuem estruturas policíclicas. Nesta classe de substâncias incluem-se certos produtos naturais (esteróides, alcalóides, terpenos, etc.) e inúmeros sistemas heterocíclicos que foram sintetizados para fins industriais ou para estudar seus comportamentos químicos e farmacológicos. Os heterociclos polinucleares podem ser obtidos mediante várias rotas. Há casos em que utilizam-se intermediários que já contenham alguns anéis pré-formados. Neste trabalho apresentaremos a síntese de um sistema heterocíclico condensado, de interesse biológico, a partir de um heterociclo simples – o tiofeno (I).

2. RESULTADOS E DISCUSSÃO

Para ilustrar esta estratégia, foi sintetizado o sistema tetracíclico inédito tieno[3'', 2'':5',6']pirido[4', 3':3,4]pirazolo[1,5-a]pirimidina (VIII) a partir do tiofeno. O esquema de síntese é apresentado na Figura 1. Em cada passo da elaboração do novo sistema heterocíclico nota-se que o produto formado é o intermediário chave (IV, V, VII) para a etapa seguinte. Foram escolhidos métodos de síntese que levaram diretamente ou em poucas reações aos sistemas desejados. Assim para a síntese de 4-hidroxitieno[2,3-*b*]piridina-5-carbonitrila (V), o método de *Goulds e Jacobs* foi aplicado[1]. O tiofeno foi nitrado. O 2-nitrotiofeno (II) obtido foi reduzido em seguida, por método químico, fornecendo 2-aminotiofeno (III) – isolado como um complexo