

Eco-friendly Conditions for the Production of 1,3-Dithianes Using Microwave Irradiation

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Abstract. The reaction of a number of aldehydes and ketones with 1,3-propanedithiol has been carried out in the absence of solvent, using microwave irradiation as the heat source. Under these conditions the corresponding 1,3-dithianes were obtained in short reaction times (5 min). In addition, a bentonitic clay was evaluated as promoter of this reaction.

Key words: Green chemistry; 1,3-dithianes; bentonitic clay; microwave irradiation.

Resumen. La reacción entre varios aldehídos y cetonas con 1,3-propaneditiol se llevó a cabo en la ausencia de disolvente, utilizando irradiación de microondas como fuente de calor. Bajo estas condiciones, se obtuvieron los correspondientes 1,3-ditianos, en tiempos cortos de reacción (5 min). Complementariamente, se evaluó la capacidad de una arcilla bentonítica como promotora de esta reacción.

Palabras clave: Química verde; 1,3-ditianos; arcilla bentonítica; radiación de microondas.

Introduction

An objective of green chemistry is to carry out reactions under conditions which are not detrimental to the environment [1], and the ideal synthesis is that, in which the target molecule is produced quantitatively in one step, from available and inexpensive starting compounds, in an environmentally acceptable process [2].

The high stability of dithioacetals and consequently the specific conditions required for their removal from masked carbonyls have afforded priceless uses of them in synthesis [3]. In addition, there are several reasons why cyclic dithioacetals in general, and 1,3-dithianes in particular, attracted the attention of synthetic chemists [4]. For example, these compounds are easily metallated with alkylolithium solutions, and the resulting carbanions can be employed as effective nucleophiles in C-C bond-forming reactions; additionally, they play an important role in the synthon and umpolung concepts [5,6], and some 1,3-dithianes have been objects of study for the anomeric effect [7,8].

After an extensive search of the literature, it was encountered that, the standard procedure for the preparation of 1,3-dithianes consists in the Lewis or Brønsted acid-catalyzed transformation of carbonylic substrates or their corresponding *O,O*-acetals with 1,3-propanedithiol [9]. Also, the reaction of 1,3-propanedithiol with *gem*-diiodo alkanes affords the access to 1,3-dithiacyclohexanes [10]. The most common catalysts employed to produce 1,3-dithianes are: HCl, HCl/ZnCl₂ [11,12], BF₃·Et₂O [12-14], *p*-toluenesulfonic acid [15], HCOOH [16], UF₆[10], SnCl₂[17], and *bis*(diphenylphosphine)methane complexes of platinum (II) [18]. The literature

also informs on the use of undesirable solvents such as CHCl₃, C₆H₆, THF, HCOOH, 1,2-trichlorotrifluorometane (Freon 113), CH₂Cl₂, C₇H₈ and Me₂CO, (*vide supra*).

Recently, for the production of a wide number of *S,S*-acetals, the employment of two eco friendly-clays KSF [19] and TAFF [20, 21] has been reported; however, these methods make use of very toxic solvents such as benzene or toluene.

It is also worth noting that microwave irradiation and solventless conditions have been employed to produce cyclic *S,S*-acetals [22-24], however, these procedures involve exchange reactions from other masked carbonylic compounds, as well as the presence of an acid as catalyst.

The aim of this work is to inform on the one-pot production of two series of 1,3-dithianes, **3a-i** and **5j-m**, under solventless conditions, using microwave irradiation as the heat source. In addition TAFF, an eco-friendly bentonitic clay [21] was evaluated as catalyst.

Results and Discussion

The reactions performed in this work are shown in Scheme 1, and the corresponding results are summarized in Table 1. As it can be seen, the reaction of aldehydes (**1a-i**) or ketones (**4j-m**) with 1,3-propanedithiol (**2**), under solventless conditions and using microwave irradiation as the energy source, gives 1,3-dithianes **3a-i** and **5j-m** in good yields, and in very short times. In addition, the comparative study, in which TAFF, an eco-friendly bentonitic clay was evaluated as catalyst (Table 1), demonstrated that an acidic promotor [21] is not required for the production of the target molecules. Moreover, it is

Table 1. Microwave production of 1,3-dithianes **3a-i** and **5j-m**

Product	With TAFF Yield ^a (Formation) ^b	Without TAFF Yield ^a (Formation) ^b
3a	92 (100)	89 (97)
3b	89 (97)	81 (90)
3c	80 (99)	78 (91)
3d	88 (95)	89 (91)
3e	86 (96)	60 (91)
3f	89 (99)	84 (99)
3g	93 (100)	89 (97)
3h	87 (97)	81 (88)
3i	84 (94)	78 (91)
5j	ε (3.8)	ε (3.2)
5k	24 (36)	27 (39)
5l	77 (98)	69 (95)
5m	ε (12)	ε (12)

^a After workup. ^bDetermined by GCMS. ^cNot determined.

worth noting that the use of microwave irradiation has been previously evaluated [22-24] for the same purpose, however, a protected carbonylic moiety and an acid-catalyst were employed; consequently, this new procedure is a complete green chemistry protocole.

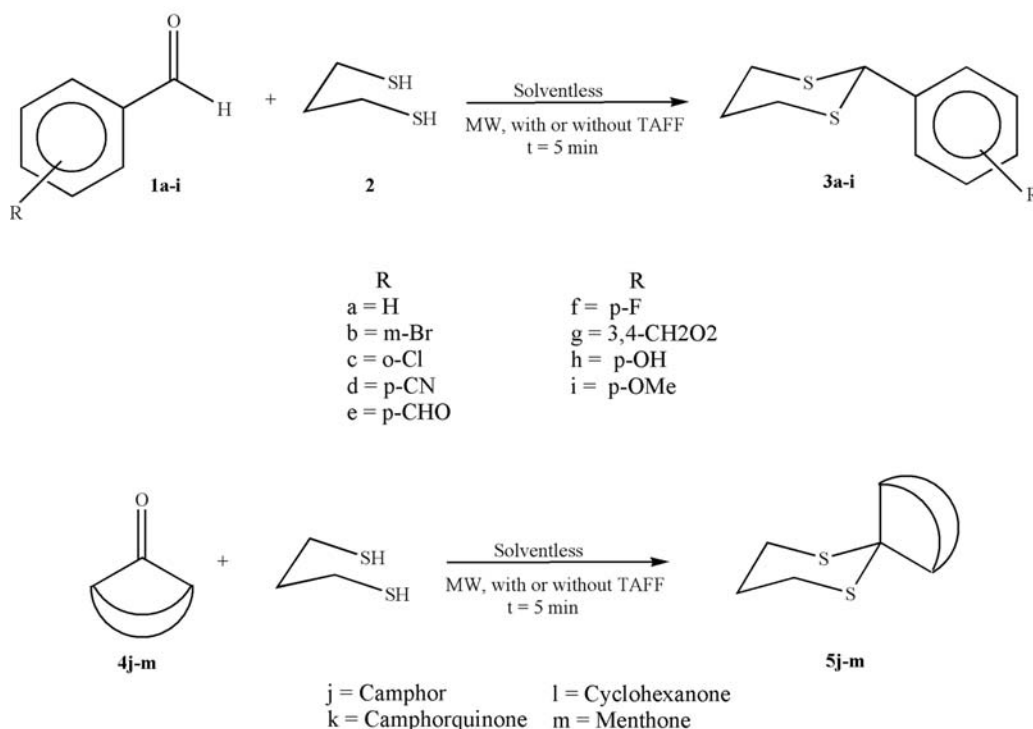
For the identification of compounds **3a-i** and **5j-m**, firstly, we envisaged by mass spectrometry [20] the presence of the molecular radical ions in agreement with the corresponding molecular weights, this in addition to analogous fragments that follow a typical fragmentation pattern for a 1,3-dithiane:

[M-43]⁺, [M-65]⁺, [M-74]⁺ and [M-75]⁺. In general, the corresponding proton nuclear magnetic resonance data of the molecules gave evidence for the presence of the 1,3-dithiane moieties, since the *S,S*-cyclic acetals showed analogous chemical shifts and coupling patterns: dtt 1.81-1.98 ppm H_a-5, dtt 2.10-2.21 ppm H_c-5, ddd 2.85-2.97 H_a-4,6, and ddd 2.90-3.18 H_e-4,6 with coupling constants of $J_{4a/4e} \sim J_{5a/5e} \sim 13-14$ Hz; $J_{4a/5a} = 10-12$ Hz; $J_{4a/5e} \sim J_{4e/5a} = 2.6-3.4$ Hz; $J_{4e,5e} = 4-6$ Hz; this in addition to the corresponding shifts and patterns of the protons in the substituents at C-2.

Finally, it is important to note that the dithianes **5j** and **5m** were produced in low quantities due to steric factors; consequently they were only identified by GCMS.

Experimental

General features: All aldehydes and ketones are commercially available (Aldrich Chemical Co.) and were employed without further purification. Camphorquinone was prepared by a previously reported procedure [25]. The TAFF, a bentonitic clay, was obtained from Tonsil Mexicana S.A de C.V., Insurgentes Sur, C.P. 01020 Mexico-City [26]. The reactions were monitored by TLC (*n*-hexane/AcOEt, 4:1) on precoated (0.25 mm) Merk silica-gel 60-F₂₅₄ aluminum sheets; the visualization of the products was done using a 254 nm UV lamp (UVP Mod UVLS-24); for the corresponding column chromatographies (flash) silica gel Merck 230-400 mesh was employed. The melting points were determined in a Fisher Scientific apparatus, and are uncorrected. The refraction index was determined

**Scheme 1**

in an Abbe Refractometer Bausch & Lomb serial No. U321141R, boiling points were determined by the Siwoloff method. The products were identified by mass spectrometry; EIMS (70 eV) spectra by direct introduction (pure compounds) were obtained using a Finnigan Mat-GCQ. The corresponding conversion percentages, were determined by GC-MS employing a Varian Saturn 4D under EI mode, equipped with a capillary column 30 m length by 0.25 mm diameter, packed with 5% phenyl and 96% dimethylpolysiloxane. The complement identification of the products was performed by ^1H NMR in a Varian Mercury XR-300 Spectrometer using CDCl_3 or DMSO-d_6 as the solvent and tetramethylsilane as internal reference.

General procedure. - A mixture of aldehyde **1a-i** or ketone **4j-m** (2 mmol) and 1,3-propanedithiol **2** (2 mmol) was placed in a reactor with a diameter of 4.4 cm, where upon it was treated during 5 min with microwave irradiation (600W) in a conventional microwave oven (Samsung, Mod. MW1040WA). Analogous experiments were performed, for comparison, in the presence of TAFF as catalytic promoter (250 mg).

2-Phenyl-1,3-dithiane (3a). White solid: mp 68-69 °C; ^1H NMR (CDCl_3 , 300 MHz) δ 1.95 (1H, dtt, H-5_a), 2.20 (1H, dtt, H-5_e), 2.90 (2H, ddd, H-4_a,6_a), 3.06 (2H, ddd, H-4_e,6_e), 5.17 (1H, s, H-2), 7.35 (5H, m, H-Ar); ^{13}C NMR (CDCl_3 , 75 MHz) δ 25.05 (C-5), 32.05 (C-4,6), 51.42 (C-2), 127.69 (C-2',6'), 128.39 (C-3',5'), 128.67 (C-4'), 139.02 (C-1'); EIMS m/z (rel. int.): 196 [M](100), 153 (7.5), 149 (3.4), 135 (7.5), 131 (21.2), 122 (21), 121 (55), 117 (5), 105 (12.8), 74 (7). Yield: 89%.

2-(3-Bromophenyl)-1,3-dithiane (3b). Yellow oil: bp 132 °C, n_D^{25} 1.560; ^1H NMR (CDCl_3 , 300 MHz) δ 1.91 (1H, dtt, H-5_a), 2.19 (1H, dtt, H-5_e), 2.93 (2H, ddd, H-4_a,6_a), 3.05 (2H, ddd, H-4_e,6_e), 5.11 (1H, s, H-2), 7.20 (2H, m, H-5',6'), 7.41 (2H, m, H-2',4'); ^{13}C NMR (CDCl_3 , 75 MHz) δ 24.89 (C-5), 31.87 (C-4,6), 50.53 (C-2), 126.73 (C-5'), 130.52 (C-6'), 131.20 (C-4'), 131.80 (C-2'), 141.45 (C-1'), 142.67 (C-3'); EIMS m/z (rel. int.): 276 (97.4), 274 (100) [M], 226 (1.5), 200 (37), 199 (9.5), 105 (47), 74 (33.5). Yield: 81%.

2-(2-Chlorophenyl)-1,3-dithiane (3c). White solid: mp 90-92 °C; ^1H NMR (CDCl_3 , 300 MHz) δ 1.91 (1H, dtt, H-5_a), 2.20 (1H, dtt, H-5_e), 2.89 (2H, ddd, H-4_a,6_a), 3.11 (2H, ddd, H-4_e,6_e), 5.64 (1H, s, H-2), 7.21 (1H, ddd, $J_{5',3'}=1.8$, $J_{5',4'}=J_{5',6'}=7.2$ Hz, H-5'), 7.30 (1H, ddd, $J_{4',6'}=1.5$, $J_{4',3'}=J_{4',5'}=7.2$ Hz, H-4'), 7.36 (1H, dd, $J_{6',4'}=1.5$, $J_{6',5'}=7.2$ Hz, H-6'), 7.68 (1H, ddd, $J_{3',4'}=7.2$, $J_{3',5'}=1.8$ Hz, H-3'); ^{13}C NMR (CDCl_3 , 75 MHz) δ 25.10 (C-5), 32.23 (C-4,6), 47.56 (C-2), 127.44 (C-5'), 129.44 (C-6'), 129.59 (C-4'), 129.62 (C-3'), 132.40 (C-2'), 136.50 (C-1'); EIMS m/z (rel. int.): 232 (32), 230 (100) [M], 165 (2.5), 156 (5.5), 155 (17), 105 (5.5), 74 (3). Yield: 78%.

2-(4-Cyanophenyl)-1,3-dithiane (3d). White solid: mp 108-110 °C; ^1H NMR (CDCl_3 , 300 MHz) δ 1.98 (1H, dtt, H-5_a), 2.20 (1H, dtt, H-5_e), 2.92 (2H, ddd, H-4_a,6_a), 3.05 (2H, ddd,

H-4_e,6_e), 5.18 (1H, s, H-2), 7.61 (4H, AA'BB', $J=6.6$ Hz, H-2',3',5',6'); ^{13}C NMR (CDCl_3 , 75 MHz) δ 24.75 (C-5), 31.69 (C-4,6), 50.62 (C-2), 112.11 (C-1'), 118.41 (C-2',6'), 128.63 (C-3',5'), 132.49 (C-4'), 144.13 (C-7'); EIMS m/z (rel. int.): 221 (100) [M], 178 (12.5), 160 (6.5), 156 (8.6), 147 (20.1), 146 (60.5), 142 (1.5), 105 (21.2), 74 (52.1). Yield: 89%.

2-(4-Formylphenyl)-1,3-dithiane (3e). White solid: mp 86-88 °C; ^1H NMR ($\text{Me}_2\text{CO-d}_6$, 300 MHz) δ 1.85 (1H, dtt, H-5_a), 2.21 (1H, dtt, H-5_e), 2.97 (2H, ddd, H-4_a,6_a), 3.18 (2H, ddd, H-4_e,6_e), 5.47 (1H, s, H-2), 7.81 (4H, AA'BB', $J=8.4$ Hz, H-2',3',5',6'), 10.04 (1H, s, H-7'); ^{13}C NMR ($\text{Me}_2\text{CO-d}_6$, 75 MHz) δ 25.92 (C-5), 32.19 (C-4,6), 51.29 (C-2), 129.42 (C-2',6'), 130.67 (C-3',5'), 130.80 (C-4'), 141.20 (C-1'), 192.38 (C-7'); EIMS m/z (rel. int.): 224 (100) [M], 181 (3.1), 177 (1), 159 (31.7), 150 (13.6), 149 (51), 105 (26), 74 (21). Yield: 60%.

2-(4-Fluorophenyl)-1,3-dithiane (3f). White solid: mp 96-98 °C; ^1H NMR (CDCl_3 , 300 MHz) δ 1.94 (1H, dtt, H-5_a), 2.15 (1H, dtt, H-5_e), 2.93 (2H, ddd, H-4_a,6_a), 3.05 (2H, ddd, H-4_e,6_e), 5.15 (1H, s, H-2), 7.45 (4H, AA'BB', $J=5.1$ Hz, H-2',3',5',6'); ^{13}C NMR (CDCl_3 , 75 MHz) δ 24.94 (C-5), 32.10 (C-4,6), 50.47 (C-2), 115.60 (C-2',6'), 129.50 (C-3',5'), 135.00 (C-1'), 160.90 (C-4'); EIMS m/z (rel. int.): 214 (100) [M], 171 (5), 153 (4), 149 (10), 140 (4), 139 (15.7), 105 (13), 74 (4). Yield: 84%.

5-((1,3-Dithian-2-yl)benzo[d]-1,3)dioxole (3g). White solid: mp 85-87 °C; ^1H NMR (CDCl_3 , 300 MHz) δ 1.98 (1H, dtt, H-5'_a), 2.18 (1H, dtt, H-5'_e), 2.85 (2H, ddd, H-4'_a,6'_a), 3.05 (2H, ddd, H-4'_e,6'_e), 5.09 (1H, s, H-2'), 5.95 (2H, s, H-2), 6.74 (1H, d, $J_{7,6}=8.5$ Hz, H-7), 6.90 (1H, d, $J_{4,6}=1.5$ Hz, H-4), 6.98 (1H, dd, $J_{6,7}=8.1$, $J_{6,4}=1.5$ Hz, H-6); ^{13}C NMR (CDCl_3 , 75 MHz) δ 24.94 (C-5'), 32.10 (C-4',6'), 51.10 (C-2'), 101.16 (C-2), 108.30 (C-4,7), 121.21 (C-6), 132.84 (C-1a,3a), 147.60 (C-5); EIMS m/z (rel. int.): 240 (62.1) [M], 197 (3.4), 193 (1), 179 (2.5), 175 (6.7), 166 (17.5), 165 (21), 161 (3.1), 105 (5), 74 (13.1). Yield: 89%.

2-(4-Hydroxyphenyl)-1,3-dithiane (3h). Brown solid: mp 146-148 °C; ^1H NMR ($\text{Me}_2\text{CO-d}_6$, 300 MHz) δ 1.81 (1H, dtt, H-5_a), 2.13 (1H, dtt, H-5_e), 2.86 (2H, ddd, H-4_a,6_a), 3.10 (2H, ddd, H-4_e,6_e), 5.24 (1H, s, H-2), 7.05 (4H, AA'BB', $J=8.7$ Hz, H-2',3',5',6'); ^{13}C NMR ($\text{Me}_2\text{CO-d}_6$, 75 MHz) δ 26.00 (C-5), 32.54 (C-4,6), 51.17 (C-2), 116.50 (C-3',5'), 129.82 (C-2',6'), 131.71 (C-1'), 158.21 (C-4'); EIMS m/z (rel. int.): 212 (78) [M], 169 (5.2), 165 (2), 151 (5.5), 147 (2), 137 (81), 105 (7.5), 74 (3). Yield: 81%.

2-(4-Methoxyphenyl)-1,3-dithiane (3i). Pink solid: mp 109-111 °C; ^1H NMR ($\text{Me}_2\text{CO-d}_6$, 300 MHz) δ 1.81 (1H, dtt, H-5_a), 2.16 (1H, dtt, H-5_e), 2.85 (2H, ddd, H-4_a,6_a), 3.11 (2H, ddd, H-4_e,6_e), 3.79 (1H, s, H-7'), 5.28 (1H, s, H-2), 7.14 (4H, AA'BB', $J=8.7$ Hz, H-2',3',5',6'); ^{13}C NMR ($\text{Me}_2\text{CO-d}_6$, 75 MHz) δ 25.96 (C-5), 32.45 (C-4,6), 51.01 (C-7'), 55.53 (C-2),

114.71 (C-3',5'), 129.73 (C-2',6'), 132.80 (C-1'), 160.46 (C-4'); EIMS m/z (rel. int.): 226 (100) [M]; 183 (3), 179 (2), 165 (4.1), 161 (10.1), 152 (29.9), 151 (63.4), 105 (17.5), 74 (18). Yield: 78%.

Spiro [1,7,7-trimethyl- bicyclo[2.2.1]-heptan-3.2'-1',3'-dithiane] (5j). EIMS m/z (rel. int.): 242 (88) [M], 199 (27), 195 (3), 181 (14), 168 (27), 167 (10), 163 (3), 105 (27), 74 (35). Formation (GC-EIMS): 3.2%.

Spiro [1,7,7-trimethyl-2-oxo- bicyclo[2.2.1]heptan-3.2'-1',3'-dithiane] (5k). Colorless oil: bp 108 °C, n_D^{25} 1.537; ^1H NMR (CDCl_3 , 300 MHz) δ 0.92 (3H, s, Me-8), 0.94 (3H, s, Me-10), 1.0 (3H, s, Me-9), 1.25 (2H, m, H-5_a,5_e), 1.90 (2H, m, H-6_a,6_e), 1.91 (1H, dtt, H-5'_a), 2.21 (1H, dtt, H-5'_e), 2.28 (1H, m, H-4), 2.90 (2H, ddd, H-4'_a,6'_a), 3.05 (2H, ddd, H-4'_e, 6'_e); ^{13}C NMR (CDCl_3 , 75 MHz) δ 9.50 (C-10), 18.80 (C-8), 19.47 (C-9), 20.64 (C-5), 24.19 (C-5'), 30.97 (C-6), 33.45 (C-4',6'), 45.01 (C-7), 48.80 (C-4), 51.90 (C-3), 59.70 (C-1), 217.07 (C-2); EIMS m/z (rel. int.): 256 (10) [M], 213 (1.5), 195 (17), 182 (3), 181 (19.5), 105 (8), 74 (1). Yield: 27%

Spiro [cyclohexan-1.2'-1',3'-dithiane] (5l). Colorless oil: bp 68 °C, η_D^{25} 1.486; ^1H NMR ($\text{Me}_2\text{CO}-d_6$, 300 MHz) δ 1.50 (6H, m, H-3',4',5'), 1.84 (1H, dtt, H-5_a), 1.91 (4H, m, H-2',6'), 2.10 (1H, dtt, H-5_e), 2.68 (2H, ddd, H-4_a,6_a), 2.90 (2H, ddd, H-4_e,6_e); ^{13}C NMR ($\text{Me}_2\text{CO}-d_6$, 75 MHz) δ 21.54 (C-3',5'), 25.5 (C-5), 25.7 (C-4'), 32.90 (C-4,6), 37.42 (C-2',6'), 49.82 (C-2'); EIMS m/z (rel. int.): 188 (100) [M], 145 (19), 127 (3.5), 114 (9.5), 113 (7.5), 105 (5), 74 (2). Yield: 69%.

Spiro [5-methyl-2-isopropyl- cyclohexan-1.2'-1',3'-dithiane] (5m). EIMS m/z (rel. int.): 244 (100) [M], 201 (10.5), 183 (2), 170 (5.5), 169 (33.5), 165 (9), 105 (7), 74 (6.5). Formation (GC-EIMS): 12%.

Conclusion

One of Fischer's contributions to the progress of organic synthesis was the notion that a functional group could be temporarily masked by means of a suitable protecting group, which could then be later specifically removed. However, even after more than a century the masking of functional groups still remains an important challenge in organic synthesis; for example, the protection of an aldehyde or a ketone is frequently a necessary step in synthetic chemistry. In this sense, the dithiane system is a common way for the protection of carbonylic moieties; however, the published procedures for this purpose usually require conditions that are hazardous to the environment, such as toxic solvents and acids. In this paper we described a solventless procedure for the one-pot

protection of carbonylic compounds, giving 1,3-dithianes, also we found that the presence of an acidic medium is irrelevant in this conditions. In addition no exchange of protecting group is occurred [23,24].

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References

- Anastas, P. T.; Williamson, T. C., in: *Green Chemistry, Frontiers in Benign Chemical Syntheses and Processes.*, Ed., Oxford University Press, California, **1998**.
- Wender, P. A.; Handy, S. L.; Wright, D. L. *Chem. Ind. London*, **1997**, 765-769.
- Luh, T. Y. *Acc. Chem. Res.* **1991**, *24*, 257-263.
- Van Niel, M. B.; Prodger, J. C. *Tetrahedron* **1989**, *45*, 7643-7677.
- Gröbel, B. T.; Seebach, D. *Synthesis* **1977**, 357-402.
- Seebach, D. *Angew. Chem. Int. Ed. Engl.* **1979**, *18*, 239-258.
- Juaristi, E.; Tapia, J.; Méndez, R. *Tetrahedron*. **1986**, *42*, 1253-1264.
- Juaristi, E.; Cuevas, G., in: *The Anomeric Effect.*, Ed., CRC Press, Inc. Boca Raton, FL, **1995**.
- Corey, E.; Seebach, D. *Org. Synth.* **1975**, *40*, 231-237.
- Olah, G. A.; Welch, J. J. *Am. Chem. Soc.* **1978**, *100*, 5396-5402.
- Autenrieth, W.; Wolff, K. *Ber.* **1899**, *32*, 1375-1388.
- Seebach, D. *Synthesis* **1969**, 17-36.
- Seebach, D.; Corey, E. J. *J. Org. Chem.* **1975**, *40*, 231-237.
- Apsimon, J.; Holmes, A. *Heterocycles* **1977**, *6*, 731-803.
- Coffen, D. L.; Bank, K. C.; Garret, P. E. *J. Org. Chem. Soc.* **1969**, *34*, 605-608.
- Eliel, E. L.; Rao, V. S.; Riddell, F. G. *J. Amer. Chem. Soc.* **1976**, *98*, 3583-3590.
- O'Neill, P.; Hegarty, A. F. *J. Chem. Soc., Chem. Commun.* **1987**, 52, 2114.
- Page, P. C. B.; Klair, S. S.; Brown, M. P.; Smith, C. S.; Maginn, S. J.; Mulley, S. T. *Tetrahedron* **1992**, *48*, 5933-5946.
- Labiad, B.; Villemin, D. *Synth. Commun.* **1989**, *19*, 31.
- Miranda, R.; Osnaya, R.; Garduño, R.; Delgado, F.; Álvarez, C.; Salmon, M. *Synth. Commun.* **2001**, *31*, 1587-1597.
- Miranda, R.; Arroyo, G.A.; Penieres, G.; Delgado, F.; Cabrera, A.; Álvarez, C.; Salmón, M. *Research Trends, Trends in Heterocyclic Chem.* **2003**, *9*, 195-235.
- Pério, B.; Dozias, M. J.; Jacquault, P.; Hamelin, J. *Tetrahedron Lett.* **1997**, *38*, 7867-7870.
- Pério, B.; Dozias, M. J.; Hamelin, J. *Org. Process R&D.* **1998**, *2*, 428-430.
- Pério, B.; Hamelin, J. *Green Chem.* **2000**, *2*, 252-255.
- Evans, W.C.; Ridgion, J. M.; Simonsen, J. L. *J. Chem. Soc.* **1934**, 137.
- A full physical and spectroscopical characterization of TAFF was recently performed: Miranda, R.; Ríos, H.; Delgado, F.; Cogordan, J.A.; Castro, M.; Salmón, M. *J. Applied. Cat.* **2003**, *244*, 217-233.

