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A GENERAL ALTERNATIVE TO OBTAIN S.S-ACETALS USING TAFF, A BENTONITIC CLAY, AS THE CATALYST*

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A GENERAL ALTERNATIVE TO OBTAIN S.S-ACETALS USING TAFF, A BENTONITIC CLAY, AS THE CATALYST*

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ABSTRACT

A one-pot general alternative to prepare dithioacetals, with excellent yields, *via* the condensation of 1,3-propanedithiol, benzyl, and *n*-butyl mercapthanes with several carbonylic compounds using a bentonitic earth as the catalyst is proposed. Also, the acidic role of the clay in the reaction

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* To the memory of Professor Álvaro Leo Ramírez.

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is discussed. The product structures were established by ^{1}H and ^{13}C NMR, as well as by the corresponding EIMS and HRMS data.

INTRODUCTION

The hydrolytic stability of dithioacetals and the highly specific conditions used for their removal from masked carbonyls have afforded invaluable applications in synthesis.[1] In this sense, there are important strategic reasons why cyclic S.S-acetals in general, and 1,3-dithianes in particular attracted the attention of synthetic chemists.[2] For instance, the above class of compounds is easily metallated with alkyllithium solutions, and the resulting carbanions employed as effective nucleophiles in C-C bond-forming reactions. In addition to its role in the synthon and umpolung concepts,[3,4] another interesting fact for some 1,3-dithianes is the presence of the anomeric effect.[5,6]

The standard procedures to prepare 1,3-dithianes involves the Lewis or Brönsted acid-catalyzed derivatization of carbonylic substrates or their corresponding O.O-acetals with 1,3-propane dithiols;[7] also, the reaction of 1,3-propanedithiol with *gem*-diiodo alkanes affords the access to 1,3-dithiacyclohexanes.[8] However, the literature reports provide scarce information for this purpose using montmorillonites.[15]

Related to our research program[16–18] on the use of TAFF, a commercial bentonitic clay,[19] as the catalyst or support of inorganic molecules, we have also provided in some cases alternatives to produce heterocyclic compounds.[16] Thus, using this clay, the aim of this work deals with the results of a set of experiments performed to achieve a general alternative for the catalytic heterogeneous preparation of S.S-acetals.

RESULTS AND DISCUSSION

Chemical

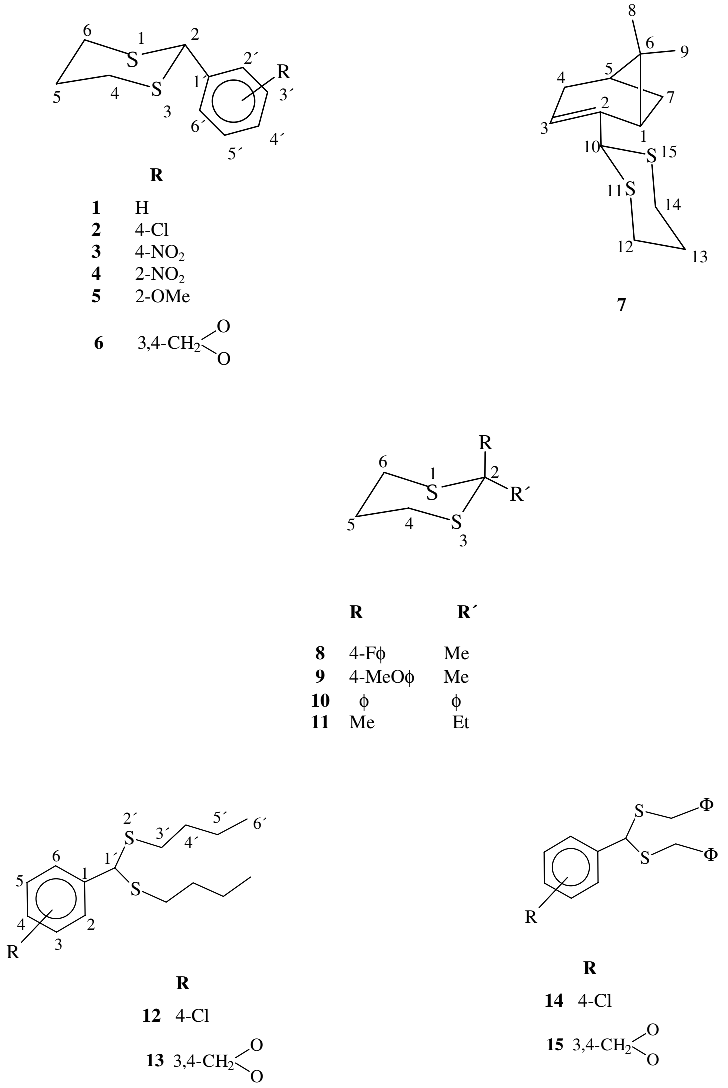
The results of a set of reactions performed with 1,3-propanedithiol and various aldehydes and ketones using TAFF as catalyst are summarized in Table 1. As it can be seen, this material is a convenient catalyst for the synthesis of useful thio-organic molecules like the 1,3-dithianes **1–11** and several acyclic dithioacetals as **12–15** (Scheme 1). These results also demonstrated that the reaction is applicable to aromatic and aliphatic aldehydes and ketones, as well as aliphatic enones. In general, the condensation

Table 1. 2-Substituted-1,3-dithianes Obtained Using TAFF as the Cayalyst

Compound	Yield (%)[a]	Melting or boiling point (°C)[b]	Mol. weight/ Elemental composition	Time (h)
1	90	68–69 (70–71)[7,10,13,15]	196.0380[c] 196.0380[d] $C_{10}H_{12}S_2$	3
2	95	81–82 (84–85)[15]	$C_{10}H_{11}S_2Cl$	3
3	95	142–143 (140–142)[10]	241.0235[c] 241.0231[d] $C_{10}H_{11}O_2NS_2$	3
4	90	122–124 (123–125)[10]	241.0226[c] 241.0231[d] $C_{10}H_{11}O_2NS_2$	3
5	60	123–125 (127–128)[10–13]	226.0292[c] 226.0486[d] $C_{11}H_{14}OS_2$	3
6	90	85–86 (84–86)[14]	240.0293[c] 240.0279[d] $C_{11}H_{12}O_2S_2$	3
7	60	Oil[e] (bp 110/100 mm Hg)	240.1002[c] 240.1006[d] $C_{13}H_{20}S_2$	3
8	95	50–51[e]	228.0451[c] 228.0443[d] $C_{11}H_{13}FS_2$	5
9	90	Oil[e] (bp 90/110 mm Hg)	240.0641[c] 240.0643[d] $C_{12}H_{16}OS_2$	5
10	90	Oil (bp 110/110 mm Hg)[9]	272.0720[c] 272.0693[d] $C_{16}H_{16}S_2$	5
11	95	Oil[11]	162.0546[c] 162.0537[d] $C_7H_{14}S_2$	5

[a]Isolated pure products; [b]uncorrected; [c]observed (HR); [d]estimated; [e]new products.

of thiols with carbonylic substrates was completed in short reaction times with very good yields in refluxing toluene. In addition, it is relevant to note several reaction advantages of this catalytic method over other reported procedures. It can be prepared without azeotropic separation of water, in general pure compounds are obtained, the work-up is easy, mild, and remarkably inexpensive.[23] Recourse to a natural, environment-friendly clay offers a valuable alternative to the numerous efficient catalytic systems that have already been proposed for this type of reaction (*Vide supra*). Moreover, the generality of this alternative is well-documented by the various examples (**1–15**) presented in this paper, together with those previously reported by us for several dithiolanes.[17] Furthermore, as it was previously mentioned, there is scant information about the employment of a



	R
1	H
2	4-Cl
3	4-NO_2
4	2-NO_2
5	2-OMe
6	3,4-$CH_2<^{O}_{O}$

	R	R′
8	4-Fϕ	Me
9	4-MeOϕ	Me
10	ϕ	ϕ
11	Me	Et

	R
12	4-Cl
13	3,4-$CH_2<^{O}_{O}$

	R
14	4-Cl
15	3,4-$CH_2<^{O}_{O}$

Scheme 1.

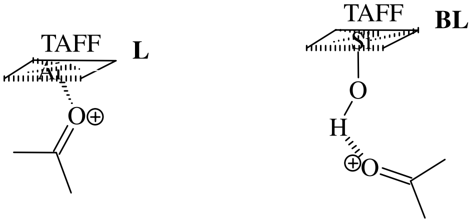
montmorillonitic material to obtain S.S-acetals; in this sense, only the KSF montmorillonite from Süd Chemie has been employed[16] for such purposes. However, it is worth mentioning that only one-seventh of the amount of TAFF is required, compared to the amount of KSF. This must be due to the great difference of surface properties between both catalysts (Table 2). From

Table 2. Comparative Surface Properties of Montmorillonitic Catalysts

Catalyst	S (cm^2/g)	Pv (cm^2/g)	Dp (Å)	pH	L	BL
TAFF[19]	198.7	0.032	77.8	3	2.52	0.25
KSF[21]	9.0	0.011	50	1.5	0.59	2.35

S specific surface area; Pv pore volume; Dp average pore diameter; pH in suspension (10% in water); L and BL Lewis and Brönsted acidity corresponding to the relative intensities of the infrared bands of adsorbed pyridine at 393°K.

the mechanistic point of view, the catalytic action of TAFF should enhance the electrophylic character of the carbonylic substrates, facilitating the nucleophilic action of the thiol; this might be due to the protonated and unprotonated active sites corresponding to the acidic Brönsted and Lewis character of the clay (Scheme 2).



Scheme 2. Enhancement of the elctrophylic character of a carbonylic substrate by means of TAFF: **L** as a Lewis and **BL** as acidic Brönsted-Löwry catalyst.

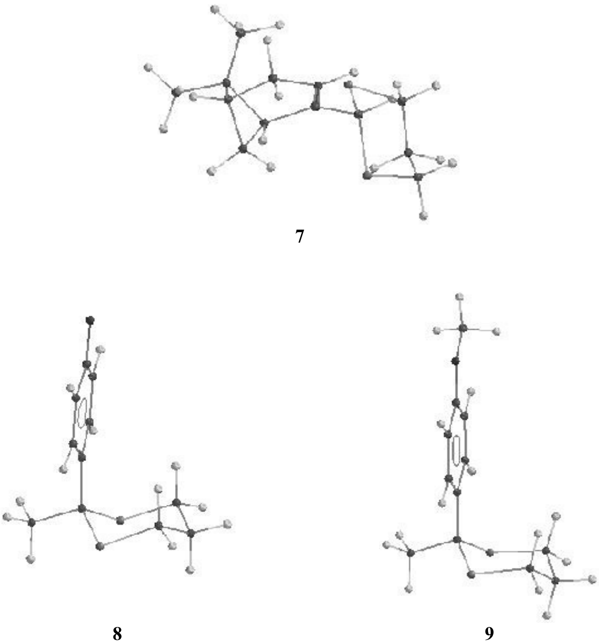
Characterization

For the structural attribution of the heterocyclic molecules, first, we envisaged by mass spectrometry that the high-resolution data of the molecular radical ions were in agreement with the exact molecular weights. This information is important since the mass measurement of an ion with sufficient accuracy provides an unequivocal identification of its elemental composition. In addition, the respective dithiane mass spectra showed analogous fragments, suggesting a common fragmentation pattern: $[M\text{-}33]^+$, $[M\text{-}43]^+$, $[M\text{-}65]^+$, $[M\text{-}74]^+$, $[M\text{-}75\text{-}H]^+$, $[M\text{-}75\text{-}15]^+$ and $C_3H_6S^+$.

When the corresponding nuclear magnetic resonance data was analyzed for the monosubstituted compounds (**1–7**), the 1,3-dithiane moieties became evident, since these S.S cyclic acetals showed analogous coupling patterns on ^1H NMR: dtt 1.81–1.99 ppm H_a-5, dtt 1.99–2.22 ppm

H_e-5, ddd 2.7–2.9 H_e 4-6, and ddd 2.9–3.15 H_a-4,6 with coupling constant values 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. In addition, these monosubstituted molecules showed anancomeric structures with H-2 in axial configuration, as demonstrated by a set of NOE-differential experiments. However, the corresponding disubstituted compounds (**8–11**) are in a dynamic equilibrium, as detected by ^{1}H NMR (H_a-4,6 collapsed with H_e-4,5 and H_a-5 with H_e-5). In general, the corresponding chemical shifts acquired by ^{13}C NMR were in agreement with the heterocyclic frame, showing signals between 22.59–26.2 and 26.05–33.5 corresponding to C-5 and C-4, 6; the C-2 signals appear between 30.58 and 46.95 ppm.

In addition to the NMR and MS data of the new molecules, semiempirical electronic structure calculations were carried out to obtain a more detailed characterization, thus the minimum energy conformations of compounds, **7**, **8**, and **9** were achieved (Scheme 3) and compared with the ^{1}H NMR experimental results, obtaining good fitness. The computations were done using the Austin Method (AM1) parameterization,[22] which has



7

8 **9**

Scheme 3. Stereostructures of new 2-substituted-1,3-ditianes: myrthenyl (7); methy, *p*-fluorophenyl (**8**); methyl, *p*-methoxyphenyl (**9**).

been previously reported to be good in order to obtain minimum energy conformations.

EXPERIMENTAL

General Features

Toluene (Aldrich) was dried prior to use (Na^0/benzophenone). The carbonylic substrates and the mercaptanes employed were also purchased from Aldrich and used as received. The catalytic material was obtained from Tonsil Mexicana and analyzed prior to use with a Siemens D-5000 X-ray difractometer using the Cu $K\alpha_1$ radiation. Purified products were characterized by spectroscopic means. ^1H NMR spectra were recorded in a Varian Gemini-300 spectrometer using $CDCl_3$ as solvent and TMS as internal reference; EIMS (70 ev) spectra and the HRMS data were obtained using JEOL MS AX 505 HA and MS-SM 102 mass spectrometers. Thin layer chromatographic analyses were performed using Merck precoated plates (silica gel 60 F_{254}, 0.25 mm); for the corresponding column chromatographies (flash) silica gel Merck 230–400 mesh was employed. The melting points were determinated in a Fisher-Johns apparatus and are uncorrected.

General Procedure

3,4-Methylene dioxybenzaldehyde (350 mg, 2.3 mmol), 5 mmol of benzylmercaptane or *n*-BuSH or 2.5 mmol of 1,3-propanedithiol were dissolved with 20 mL of anhydrous toluene and refluxed (105°C/585 mm Hg) in the presence of 250 mg of TAFF during 3 h. The reactions were monitored by TLC (*n*-hexane/EtOAc 7:3; $CeSO_4$ 1% 2N H_2SO_4), the reaction mixtures were filtered over celite and the resulting solutions washed with NaOH 10% (3 × 20 mL) then water (3 × 20 mL) and dried (Na_2SO_4). Finally, the solvent was removed under vacuum and the residue, if necessary (TLC), was purified by column chromatography.

Spectroscopic and physical data of pure isolated products

Compound 1. Yield 90%; m.p.: 68°–69°C; MW [elemental composition]: 196.038[a]/196.0380[b] [$C_{10}H_{12}S_2$]; EIMS *m/z* (ra %): 196 (100) $[M]^+$, 163 (5) $[M-33]^+$, 153 (12) $[M-43]^+$, 131 (36) $[M-65]^+$, 122 (83) $[M-74]^+$; ^1H NMR: 7.49–7.25 (m, 5H, Ar-H), 5.19 (s, 1H, H-2), 3.07 (ddd, 2H, H_a-4, 6), 2.92

(ddd, 2H, H_e-4, 6), 2.2 (dtt, 1H, H_e-5), 1.95 (dtt, 1H, H_a-5); ^{13}C NMR: 25.05 (C-5), 32.04 (C-4, 6), 51.41 (C-2), 127.69 (C-2′, 6′), 128.38 (C-3′, 5′), 128.67 (C-4′), 139.05 (C-1′).

Compound 2. Yield 95%; m.p.: 81°–82°C; MW [elemental composition] [$C_{10}H_{11}S_2Cl$]; EIMS m/z (ra %): 232 (40) $[M+2]^+$, 230(100) M^+, 197 (5) $[M-33]^+$, 187 (7) $[M-43]^+$, 165 (22) $[M-65]^+$, 156 (71) $[M-74]^+$; ^{1}H NMR: 7.49–7.30 (AA′BB′, 4H, Ar-H), 5.18 (s, 1H, H-2), 3.06 (ddd, 2H, H_a-4, 6), 2.93 (ddd, 2H, H_e-4, 6), 2.19 (dtt, 1H, H_e-5), 1.95 (dtt, 1H, H_a-5).

Compound 3. Yield 95%; m.p.: 142°–143°C; MW [elemental composition]: 241.0235^a/241.0231^b [$C_{10}H_{11}O_2NS_2$]; EIMS m/z (ra %): 241 (100) $[M]^+$, 208 (3) $[M-33]^+$, 176 (12) $[M-65]^+$, 167 (12) $[M-74]^+$; ^{1}H NMR: 7.95 (AA′BB′, 4H, Ar-H), 5.26 (s, 1H, H-2), 3.08 (ddd, 2H, H_a-4, 6), 2.96 (ddd, 2H, H_e-4, 6), 2.21 (dtt, 1H, H_e-5), 1.95 (dtt, 1H, H_a-5); ^{13}C NMR: 26.01 (C-5), 32.51 (C-4, 6), 51.90 (C-2), 125.60 (C-2′, 6′), 132.00 (C-3′, 5′), 147.15 (C-1′), 147.50 (C-4′).

Compound 4. Yield 90%; m.p.: 122°–124°C; MW [elemental composition]: 241.0226^a/241.0231^b [$C_{10}H_{11}O_2NS_2$]; EIMS m/z (ra %) 241 (22) $[M]^+$, 167 (12) $[M-74]^+$, 167 (12) $[M-74]^+$, 166 (42) $[M-74-H]^+$, 106 (100) $[C_3H_6S_2]^+$; ^{1}H NMR: 7.95 (dd, 1H, $J_{o, m}$, H-3′), 7.90 (dd, 1H, $J_{o, m}$, H-6′), 7.65 (ddd, 1H, $J_{o, m}$, H-5′), 7.45 (ddd, $J_{o, m}$, H-4′), 5.91 (s, 1H, H-2), 3.11 (ddd, 2H, H_a-4, 6), 2.92 (ddd, 2H, H_e-4, 6), 2.22 (dtt, 1H, H_e-5), 1.97 (dtt, 1H, H_a-5); ^{13}C NMR: 24.40 (C-5), 32.50 (C-4, 6), 45.90 (C-2), 122.90 (C-4′), 128.90 (C-5′), 132.81 (C-6′), 134.20 (C-3′), 148.32 (C-1′), 148.48 (C-2′).

Compound 5. Yield 60%; oil; MW [elemental composition]: 226.0292^a/226.0486^b [$C_{11}H_{14}OS_2$]; EIMS m/z (ra %): 226 (100) $[M]^+$, 193 (5) $[M-33]^+$, 161 (6) $[M-65]^+$, 152 (51) $[M-74]^+$; ^{1}H NMR: 7.61 (dd, 1H, $J_{o, m}$, H-6′), 7.27 (ddd, 1H, $J_{o, o, m}$, H-4′), 6.98 (ddd, 1H, $J_{o, o, m}$, H-5′), 6.89 (dd, 1H, $J_{o, m}$, H-3′), 5.72 (s, 1H, H-2), 3.88 (s, 3H, OMe), 3.10 (ddd, 2H, H_a-4, 6); 2.89 (ddd, 2H, H_e-4, 6), 2.21 (dtt, 1H, H_e-5), 1.98 (dtt, 1H, H_a-5); ^{13}C NMR: 26.15 (C-5), 33.01 (C-4, 6), 44.15 (C-2), 56.45 (-OMe), 110.62 (C-3′), 121.85 (C-5′), 127.95 (C-2′), 129.85 (C-6′), 131.2 (C-4′), 156.15 (C-1′).

Compound 6. Yield 90%; m.p.: 85°–86°C; MW [elemental composition]: 240.0293^a/240.0279^b [$C_{11}H_{12}O_2S_2$]; EIMS m/z (ra %): 240 (90) $[M]^+$, 207 (3) $[M-33]^+$, 197 (5) $[M-43]^+$, 175 (8) $[M-65]^+$, 166 (100) $[M-74]^+$; ^{1}H NMR: 6.95 (dd, 1H, $J_{o, m}$, H-6′), 6.91 (d, 1H, J_m, H-2′), 6.74 (d, 1H, $J_{o,}$ H-5′), 5.93 (s, 2H, CH_2O_2), 5.07 (s, 1H, H-2), 3.15 (ddd, 2H, H_a-4, 6); 2.91 (ddd, 2H, H_e-4, 6), 2.19 (dtt, 1H, H_e-5), 1.92 (dtt, 1H, H_a-5); ^{13}C NMR: 25.05 (C-5), 32.16 (C-4, 6), 51.17 (C-2), 101.25 (-CH_2O_2), 108.38 (C-2′, 5′), 121.32 (C-6′), 132.81 (C-3′, 4′), 147.95 (C-1′).

Compound 7. Yield 60%; oil; MW [elemental composition]: 240.1002^a/240.1006^b [$C_{13}H_{20}S_2$]; EIMS m/z (ra %): 225 (4) $[M-15]^+$, 207 (3) $[M-33]^+$, 197 (46) $[M-43]^+$, 166 (11) $[M-74]^+$, 165 (62) $[M-74-H]^+$; ^{1}H NMR: 5.71 (m, 1H, H-3), 4.62 (s, 1H, H-10), 2.92 (m, 4H, H-12, 14), 2.41 (m, 1H, H-1), 2.31 (m, 1H, H_e-7), 2.11 (m, 3H, H-5, 13), 1.84 (m, 2H, H-4), 1.32 (s, 3H, Me-9), 1.20 (d, 1H, H_a-7, J=10 Hz); 0.89 (s, 3H, Me-8); ^{13}C NMR: 144.72 (C-2), 121.06 (C-3), 52.03 (C-10), 44.80 (C-1), 40.31 (C-5), 37.95 (C-4), 31.61 (C-6), 31.03 (C-7), 30.62 (C-12, 14), 27.07 (C-9), 25.81 (C-13), 21.30 (C-8).

Compound 8. Yield 95%; m.p.: 50°–51°C MW [elemental composition]: 228.0451[a]/228.0443[b] [$C_{11}H_{13}FS_2$]; EIMS m/z (ra %): 228 (67) $[M]^+$, 213 (7) $[M-15]^+$, 195 (8) $[M-33]^+$, 185 (5) $[M-43]^+$, 154 (100) $[M-74]^+$, 139(96) $[M-74-15]^+$; ^{1}H NMR: 7.99–7.15 (AA′BB′, 4H, Ar-H), 2.69 (m, 4H, H-4, 6), 1.92 (m, 2H, H-5), 1.76 (s, 3H, Me); ^{13}C NMR: 24.56 (C-5), 28.04 (C-4, 6), 32.79 (Me), 53.28 (C-2), 115.14 (C-2′, 6′; J = 20.8 Hz), 129.65 (C-3′, 5′; J = 7.7 Hz), 139.55 (C-1′), 161.17 (C-4′; J = 248.8 Hz).

Compound 9. Yield 90%; oil; MW [elemental composition]: 240.0641[a]/240.0643[b] [$C_{12}H_{16}OS_2$]; EIMS m/z (ra %): 240(81) $[M]^+$, 225(11)$[M-15]^+$, 207 (15)$[M-33]^+$, 197 (3) $[M-43]^+$, 166(100) $[M-74]^+$, 151(75) $[M-74-15]^+$; ^{1}H NMR: 7.80–6.32 (AA′BB′, 4H, Ar-H), 3.75 (s, 3H, **OMe**), 2.65 (m, 4H, H-4, 6), 1.87 (m, 2H, H-5), 1.76 (s, 3H, C_2-**Me**); ^{13}C NMR: 22.59 (C-5), 24.51 (C-4, 6), 27.88 (C_2-**Me**), 53.14 (C-2), 54.99 (**OMe**), 113.46 (C-3′, 5′), 128.75 (C-2′, 6′), 135.49 (C-1′), 158.30 (C-4′).

Compound 10. Yield 90%; oil; b.p 110°C; MW [elemental composition]: 272.0720[a]/272.0693[b] [$C_{16}H_{16}S_2$]; EIMS m/z (ra %): 272 (46) $[M]^+$, 229 (3) $[M-43]^+$, 211 (8) $[M-61]^+$, 198 (100) $[M-74]^+$, 165 (95), 121 (45) $[M-74-77]^+$; ^{1}H NMR: 7.90–7.15 (m, 10H, Ar-H), 2.78 (m, 4H, H-4, 6), 1.99 (m, 2H, H-5); ^{13}C NMR: 24.34 (C-5), 29.23 (C-4, 6), 62.65 (C-2), 127.41–129.18 (Ar).

Compound 11. Yield 95%; oil; MW [elemental composition]: 162.0546[a]/162.0537[b] [$C_7H_{14}S_2$]; EIMS m/z (ra %): 163(7) $[M+H]^+$, 147(7) $[M-15]^+$, 133 (3) $[M-29]^+$, 119 (3) $[M-43]^+$, 106 (100) $[C_3H_6S_2]^+$ ^{1}H NMR: 2.70 (m, 4H, H-4, 6), 1.81 (m, 4H, H-5 and **CH**$_2$Me), 1.45 (s, 3H, C_2-**Me**), 0.89 (t, 3H, CH_2**Me**); ^{13}C NMR: 8.74 (CH_2**Me**), 25.04 (C-5), 26.06 (**CH**$_2$-Me), 26.82 (C_2-**Me**), 33.92 (C-4, 6).

Compound 12. Yield 75%; oil; EIMS m/z (ra %): 304 (0.3) $[M+2]^+$, 302 (1) $[M]^+$, 247 $[M+2-57]^+$, 245 $[M-57]^+$, 215 (33) $[M+2-SBu]^+$, 213 (100) $[M-S{\cdot}Bu]^+$, 157 (24) $[C_7H_5SCl]^+$; ^{1}H NMR: 7.45–7.20 (AA′BB′, 4H, Ar-H), 4.82 (s, 1H, **CH**S.S), 2.54 (m, 4H, 2C**H**$_2$S), 0.88 (t, 6H, 2**CH**$_3$).

Compound 13. Yield 70%; oil; EIMS m/z (ra %): 312 (1) $[M]^+$, 255 (3) $[M-57]^+$, 223 (100) $[M-SBu]^+$, 167 (28) $[M-SBu-56]^+$; ^{1}H NMR: 7.01 (d, 1H, J_m, H-2) 6.86 (dd, 1H, $J_{o,\,m}$, H-6), 6.72 (d, 1H, J_o, H-5), 5.95 (s, 2H, **C**H$_2$O$_2$), 4.79 (s, 1H, C**H**S.S), 2.54 (m, 4H, 2C**H**$_2$S), 1.49 (m, 8H, 2C**H**$_2$C**H**$_2$), 0.88 (t, 6H, 2C**H**$_3$).

Compound 14. Yield 80%; m.p.: decompose; EIMS m/z (ra %): 372 (1) $[M+2]^+$, 370 (3) $[M]^+$, 281 (2) $[M+2-91]^+$, 279 (6) $[M-91]^+$, 249 (25)

$[M+2\text{-}SCH_2\phi]^+$, 247 (76) $[M\text{-}SCH_2\phi]^+$, 91 (100) $[C_7H_7]^+$; ^1H NMR: 7.35–7.10 (m, 14H, **Ar-H**), 4.42 (s, 1H, **CH**S.S), 3.67 (AB, 4H, J = 13.5 Hz, $2C\mathbf{H}_2\phi$).

Compound 15. Yield 80%; m.p.: 66°–68°C; EIMS m/z (ra %): 380 (1) $[M]^+$, 289 (7) $[M\text{-}91]^+$, 257 (100) $[M\text{-}SCH_2\phi]^+$; 91 (90) $[C_7H_7]^+$; ^1H NMR: 7.41–6.63 (m, 13H, Ar-**H**), 5.83 (s, 2H, $C\mathbf{H}_2O_2$), 4.36 (s, 1H, $C\mathbf{H}S_2$), 3.64 (AB, 4H J = 13.5 Hz, $2C\mathbf{H}_2\phi$).

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19. Tonsil Actisil FF (TAFF), a commercial Mexican bentonitic clay, is easily available from Tonsil Mexicana S. A. de C. V. Mexico City, Mexico at US$ 1.30/kg. Examined with x-ray fluorescence, this clay proved to have the following composition (in percent): SiO_2, 74.5; Al_2O_3, 9.3; MgO, 0.4; Fe_2O_3, 1.3; CaO, 4.0; K_2O, 0.4; TiO_2, 0.4; H_2O, 9.7. When x-ray thermodiffractograms were run, the laminar structure was found to be unstable above 150°C. Quartz and cristobalite are also important components in the clay composition as observed by x-ray diffraction. The corresponding BET surface area was $198.718\,m^2g^{-1}$ and the pore volume and average pore diameter were $32.04 \times 10^{-2}\,cm^3\,g^{-1}$ and 77.8 Å, respectively. It is worth mentioning that a detailed characterization of the clay (^{29}Si and ^{27}Al MAS-NMR, SEM, IR-Py, DTA, and TG, H_o) is under review. Miranda, R.; Ríos, H.; Salmón, M.; Cogordán, J.A.; Cabrera, A. J. Appl. Cat. **2000**.
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