Heteroatom Chemistry
Volume 15, Number 1, 2004

Promotion of 1,3-Dithiolanes Using a Bentonitic Clay as Catalyst

J. M. Aceves,[1] G. A. Arroyo,[1] Y. M. Vargas,[1] R. Miranda,[1]
A. Cabrera,[2] and F. Delgado[3]

[1] *Departamento de Ciencias Químicas, Facultad de Estudios Superiores Cuautitlán, Universidad Nacional Autónoma de México, Avenida 1 de Mayo s/n, Cuautitlán Izcalli, Estado de México, CP 54740*

[2] *Instituto de Química, Universidad Nacional Autónoma de México, Circuito Exterior, Ciudad Universitaria, Coyoacán, México, D.F., CP 04510*

[3] *Departamento de Química Orgánica, Escuela Nacional de Ciencias Biológicas, Instituto Politécnico Nacional, Prolongación Carpio y Plan de Ayala, Casco de Santo Tomás, México, D.F., CP 11340*

Received 10 July 2003

ABSTRACT: *The reactions between 1,2-ethandithiol with several carbonylic compounds to form the corresponding 1,3-dithiolanes were performed using a natural clay as promotor. The target molecules are used as reagents to obtain fine chemicals, herbicides, fungicides, and pharmaceutical compounds among others applications. A kinetic study of camphorquinone and 1,2-ethandithiol showed a first-order dependence with 1,2-ethandithiol as well as with camphorquinone. The substrate transformation in percent was found to be dependent with the reaction time, the amount of catalyst, and the reagents concentration.* © 2003 Wiley Periodicals, Inc. Heteroatom Chem 15:71–76, 2004; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.10215

INTRODUCTION

The 1,3-dithiolanes are useful starting materials for the preparation of herbicides, fungicides, polymers, pharmaceuticals, flavors, and fine chemicals [1,2]. Of particular interest is their employment to protect the carbonyl group and as intermediates in the synthesis of organic sulfur compounds [2]. There are many general methods for the preparation of dithiolanes involving different reagents and catalysts, such as H·Y zeolite, $FeCl_3$, nafion, and more commonly BF_3; however, these catalysts have restrictions due to the pollution and their high cost [3]. In view of these considerations, the use of natural and modified clays as catalytic promoters provides important and attractive alternatives [4]. As part of our research work [5–6], TAFF, a commercial bentonitic clay [3], has long being employed by us as a catalyst and as a support of inorganic molecules in order to promote organic reactions, such as the promotion of oxathiolanes, ketonic dithiolanes, and trioxanes. Thus, the aim of this paper is to describe the preparation of several 1,3-dithiolanes with various carbonyl substrates in the presence of 1,2-ethandithiol, using the acidic clay as catalyst, in addition to a kinetic study for the preparation of the β-dithiolane of camphorquinone.

RESULTS AND DISCUSSION

The results of several experiments performed with ethandithiol and a set of aldehydes and ketones,

---

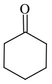
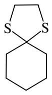
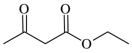
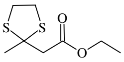
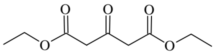
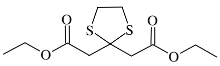
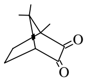
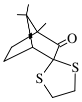
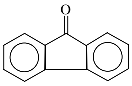
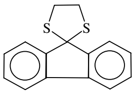
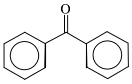
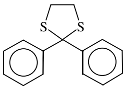
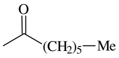
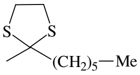
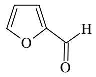
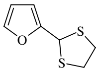
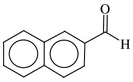
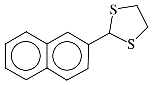
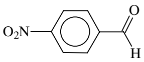
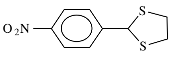
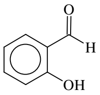
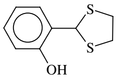
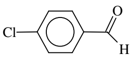
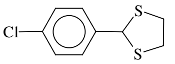
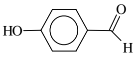
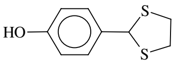
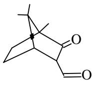
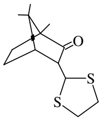
Correspondence to: J. M. Aceves; e-mail: aceves_h@yahoo.com.mx.

Contract grant sponsor: DGAPA-UNAM PAPIIT IN.
Contract grant number: 208202.

using TAFF as catalyst and anhydrous toluene as solvent, are summarized in Table 1. The target molecules are obtained in good yields and at short reaction times. In general, the compounds obtained were pure and the work-up procedure was simple, since only one spot was detected on thin-layer chromatography (TLC). The employment of the bentonitic clay thus is a good alternative for the promotion of 1,3-dithiolanes.

In order to probe the catalytic effect of the clay, the coupling reaction of ethandithiol with camphorquinone was inhibited by adding different amounts of pyridine. The results suggested the coordination of the pyridine with the Al^{3+} centers in

TABLE 1 Reaction Time and Dithiolane Formation Yields from Different Carbonyl Substrates, Using Ethandithiol as Reagent and TAFF as the Catalyst

Substrate	*Dithiolane*	*Reaction Time (h)*	*Yield*[a] *(%)*
		3	99
		4	75
		5	60
		5	80
		3	90
		3	90
		2	90
		2	95
		2	90
		2	90
		2	60
		2	90
		2	60
		3	60

[a] The yields are of pure isolated products.

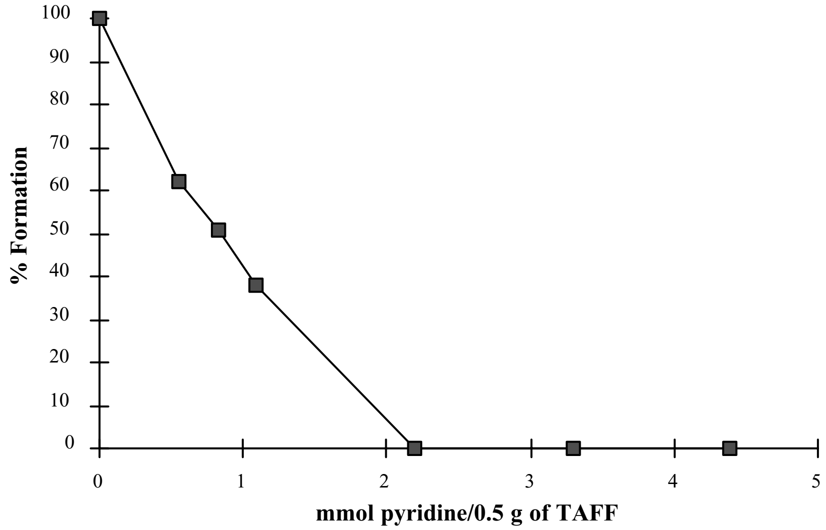


FIGURE 1 Pyridine as inhibitor of the generation of the β-dithiolane of the camphorquinone. Each point is the average of three experiments.

the montmorillonitic frame, reducing the Lewis acid sites of the clay, as shown in Fig. 1.

In addition, several reactions carried out without catalyst yielded negative results. When comparing TAFF's catalytic activity with that of Al_2O_3, SiO_2, and $SnCl_2$, it was demonstrated that only the clay produces the dithiolanes in quantitative amounts.

In this sense, Fig. 2 shows the effect of the catalyst concentration on the formation of 1,3-dithiolane, following the optimized reaction conditions when a 100% product formation was obtained. Reaction of ethandithiol (40 mmol) with 550 mg TAFF and 20 mmol camphorquinone for 5 h yields products detected by using a GC-MS. Additionally, in order to optimize the reaction time of the process, an experiment was carried out by determining the formation of 3-dithiolane as time function; in this regard, Fig. 3 shows the plot of dithiolane yield vs. time. A 100% transformation of the substrate was obtained after an optimum reaction time of 5 h.

The effect of the ethandithiol concentration is presented in Fig. 4, which shows the plot of the dithiolane yield vs. time by changing the amount of ethandithiol and maintaining the quinone concentration constant in order to determine the initial reaction rate (V_0). On plotting log V_0 vs. log dithiolane concentration, a straight line with slope 1.05 was obtained.

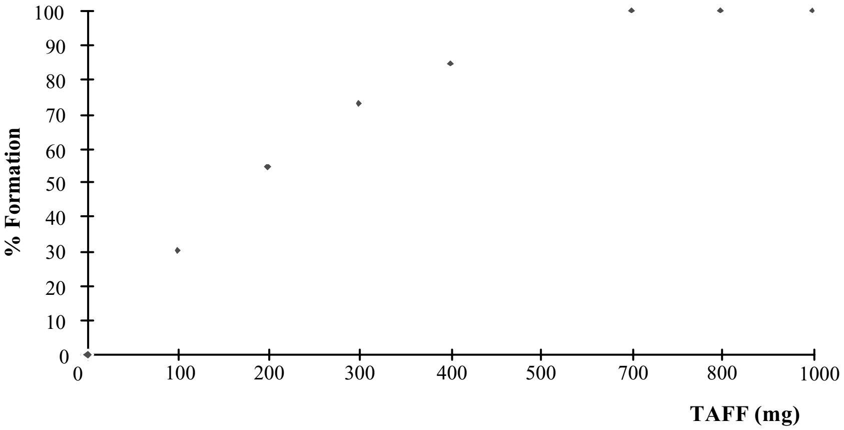


FIGURE 2 Effect of catalyst concentration on the formation of 1,3-dithiolane of camphorquinone; temperature, 105°C; camphorquinone, 20 mmol; ethandithiol, 40 mmol; reaction time, 5 h. Each point is the average value of three experiments.

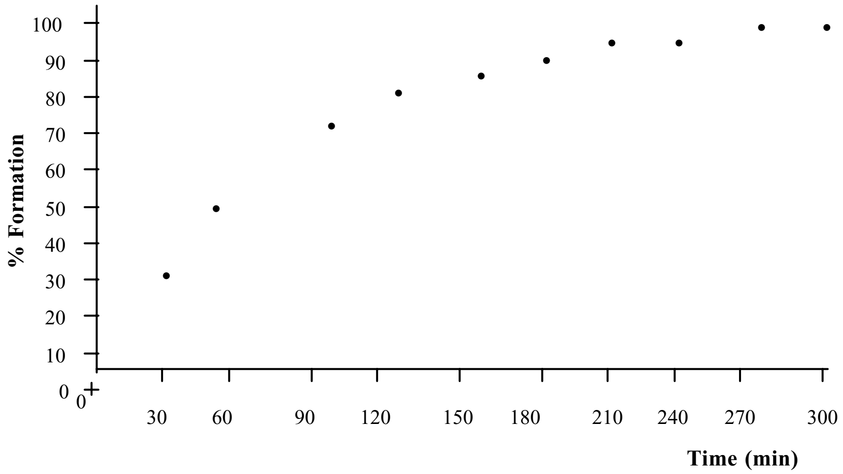


FIGURE 3 Formation of the 3-dithiolane of camphorquinone as function of time; temperature, 105°C; ethandithiol, 40 mmol; camphorquinone, 20 mmol; TAFF, 550 mg. Each point is the average value of three experiments.

A similar method was applied to study the effect of quinone concentration, obtaining an order of 1 for this experiment (Fig. 5).

EXPERIMENTAL

Toluene (Aldrich) was dried prior to use (Na/benzophenone). The carbonyl substrates and the ethandithiol employed were also purchased from Aldrich and used as received. Camphorquinone was prepared by a previously reported procedure [5]. The natural clay was obtained from Tonsil Mexicana S.A. de C.V. and analyzed prior to use with a Siemens D-5000 X-ray diffractometer using the Cu $K\alpha_1$ radiation. The Lewis acid character was confirmed with a Perkin-Elmer 1600 series FTIR spectrometer, by using the IR pyridine coordination method [7]. Purified products were characterized by spectroscopic means: ^{1}H NMR spectra were recorded in a Varian FT-200 spectrometer using CDCl$_3$ as solvent

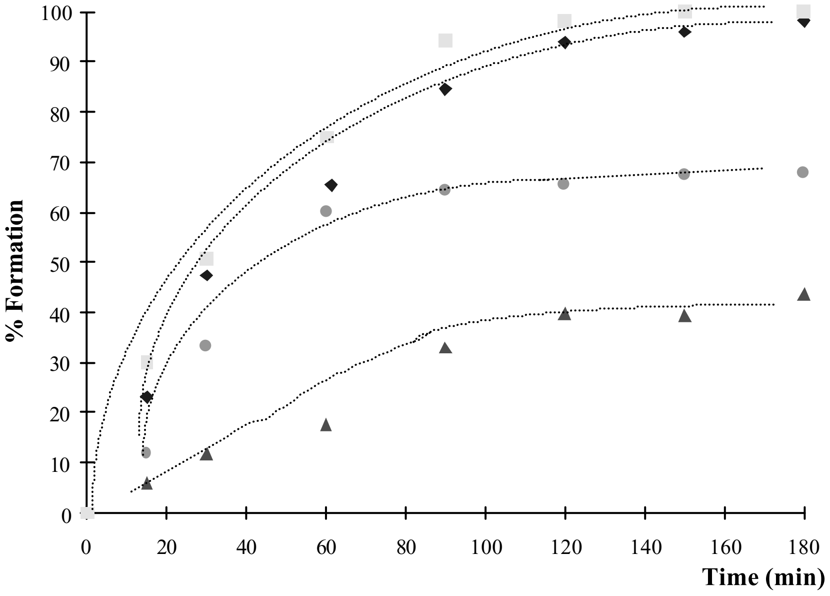


FIGURE 4 Dithiolane formation as function of the time, maintaining constant (20 mmol) the initial quantity of camphorquinone and varying the initial quantities of ethandithiol: 10 (▲), 20 (●), 40 (◆), and 50 (■) mmol. Each point is the average value of three experiments.

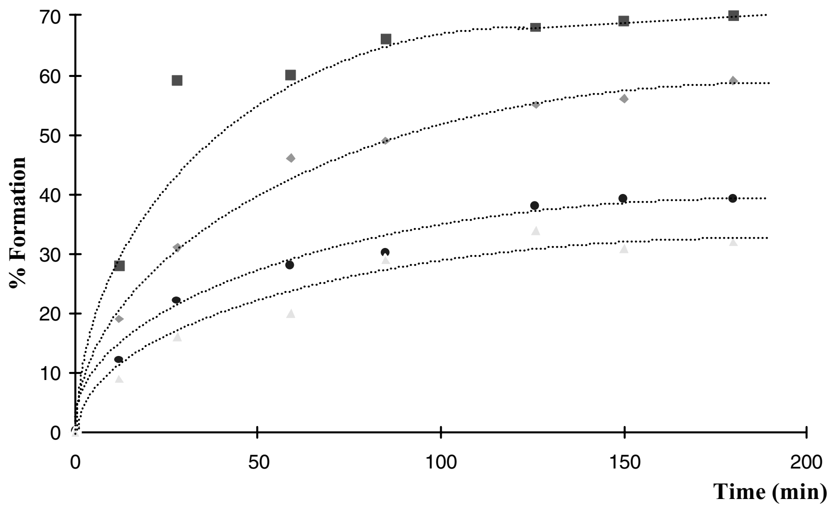


FIGURE 5 Dithiolane formation vs. reaction time, maintaining the initial quantity of ethandithiol constant (20 mmol) and initial quantities of camphorquinone (in mmol): 10 (■), 20 (▲), 30 (●), and 40 (◆). Each point is the average value of three experiments.

and TMS as internal reference; EIMS (70 eV) spectra were obtained using a HP5985 B and a JEOL JMS AX505HA mass spectrometer. For the kinetic experiments a Polyscience Corporation Temperature Controller Model 73 was employed. The corresponding percentage formation values were acquired by a Varian gas chromatograph model Star 3400 equipped with a flame ionization detector and a 30 m × 0.53 mm column packed with polyethyleneglycol. Thin-layer chromatography analysis was performed using Merck precoated plates (silica gel 60 F254, 0.25 mm), for which the corresponding chromatographic column silica gel 60 Merck 70-230 was employed.

Typical Reaction Example

Camphorquinone (2.42 g, 10 mmol) and 1,2-ethandithiol (1.2 g, 12.7 mmol) in 10 ml of anhydrous toluene were refluxed for 5 h in presence of 250 mg of activated bentonite. The reaction was monitored by TLC (*n*-hexane/EtOAc 7:3), and the reaction mixture was filtered over celite and the solution washed with NaOH 5% (2 × 20 ml) and dried (Na_2SO_4). The solvent was removed under vacuum and the residue purified by chromatographic column yielding 80% of pure β-dithiolane. In other experiments these amounts were optimized.

Inhibition of a Catalyst

A set of experiments using pyridine as inhibitor were accomplished; thus different ratios of mmol py/g TAFF (0.274, 0.549, 0.8241, 1.17, 1.175, 2.31, 4.63, 6.95, and 9.26) were tested; the concentrations of camphorquinone and ethandithiol were 2 and 4 mmol respectively, and 5 h was the reaction time (Fig. 1).

Formation of Camphorquinone β-Monodithiolane with Different Quantities of Catalyst

Various quantities (0–1000 mg) of TAFF were assayed. The reflux time was 5 h and the camphorquinone and ethandithiol concentrations were 20 mmol and 40 mmol, respectively (Fig. 2).

β-Monodithiolane of Camphorquinone Formation as Time Function

Several samples from a typical reaction were initially monitored, at 2.5, 5.0, 7.5, 15.0, and 30 min, and after that with 30 min intervals for 5 h using 540 mg of TAFF. The camphorquinone and ethandithiol concentrations were maintained at 20 mmol and 40 mmol (Fig. 3).

Determination of Ethandithiol Partial Reaction Order

The camphorquinone concentration was constant (20 mmol), a set of four experiments (10, 20, 30, and 50 mmol) of ethandithiol, 540 mg clay during 3 h, in order to know the partial reaction order of ethandithiol was performed; since the initial rate method was employed, samples for each reaction time at 2.5, 5, 7.5, 15, 30, 60, 90, 150, and 180 min were analyzed (Fig. 4).

Determination of the Camphorquinone Partial Reaction Order

In order to determine the camphorquinone partial reaction order, the initial rates method was also used. The ethandithiol concentration was maintained constant (20 mmol) while the camphorquinone concentration was assayed from 20 to 60 mmol; the quantity of TAFF in each case was 540 mg and the samples were analyzed at 2.5, 5, 7.5, 15, 30, 60, 90, 150, and 180 min (Fig. 5).

CONCLUSIONS

The reaction order for the camphorquinone and the ethandithiol was 1 for both of them and the clay employed proved to be a convenient catalyst to promote the preparation of 1,3-dithiolanes. Besides, there is a maximum pyridine concentration for total inhibition of the clay catalytic effect. Thus, it had been proven that this method is an easy one-pot work-up procedure and an effective alternative for the dithiolane preparation reaction under mild conditions.

ACKNOWLEDGMENT

Mr. Draucin Jiménez, A. Becerril, and P. García Estrada are acknowledged for technical assistance.

REFERENCES

[1] (a) Aggarwal, V.; Lightower, M. Phosphorus, Sulfur Silicon 1993, 74, 407; (b) Love, B.; Chao, L. Synth Commun 1993, 23, 3073; (c) Nakazawa, H.; Ohtsuka, M.; Matsuda, H. Eur Patent Appl. EP 308 909, 1987; (d) Soc, A.; Kanna, H.; Hasegawa, N.; Mihagi, Y. Eur Patent Appl EP 218 736, 1985.

[2] Labiad, B.; Villemin, D. Synth Commun 1989, 19, 31.

[3] The Tonsil Actisil FF (TAFF) commercial bentonitic clay was purchased from Tonsil Mexicana S. A. de C. V. Insurgentes Sur 1971, CP. 01020 Ciudad de México at US \$1.35/kg vs. [$ZnCl_2$ 99.99%, US \$2640.00/kg, $AlCl_3$ 99.99%, US \$137.20/kg, $TiCl_2$ 99.98% US \$21,900.00/kg, $BF_3 \cdot Et_2O$ US \$62.20/l, $FeCl_3$ US \$3958.00/kg, Clay K 10 US \$22.30/kg, Clay K SF US \$22.30, taken from Aldrich 1995–1997, Catalogue]; analyzed with a Phillips spectrometer using Cu Kα radiation; the X-ray fluorescence analyses proved to have the following composition (in %): MgO, 2.11; Al_2O_3, 8.55; SiO_2, 75.34; CaO, 4.72; K_2O, 2.93; TiO_2, 1.03; MnO_2, 0.03; Fe_2O_3, 6.42; CuO, 0.01; ZnO, 0.02; SeO_2, 0.002; Rb_2O, 0.032; SrO, 0.129. The specific surface obtained was 190 m^2/g (BET method, N_2); in addition, quartz and cristobalite are also important components.

[4] Lazlo, P. J Phys Org Chem 1998, 11, 356.

[5] (a) Delgado, F.; Tamariz, J.; Zepeda, G.; Landa, M.; Miranda, R.; García, J. Synth Commun 1995, 25, 753; (b) Salmón, M.; Zavala, N.; Cabrera, A.; Cárdenas, J.; Gaviño, R.; Miranda, R.; Martínez, M. J Mol Cat 1995, 104, L127; (c) Cabrera, A.; Peón, J.; Velasco, L.; Miranda, R.; Salmón, A. J Mol Cat 1995, 104, L5; (d) Penieres, G.; Miranda, R.; García, J. G.; Aceves, J. M.; Delgado, J. Heterocycl Commun 1996, 2, 401; (e) Miranda, R.; Aceves, J. M.; Gutierrez, C.; Martínez, R.; Delgado, F.; Cabrera, A.; Salmón, M. Heterocyclic Commun 1997, 3, 147, and cites therein.

[6] Miranda, R.; Arroyo, G. A.; Penieres, G.; Salmón, M.; Cabrara, A.; Aluarez, C.; Delgado, F. Heterocyclic Preparative Chemistry 1980–2003, *Research Trends*, in press (2003).

[7] Gervais, H. P.; Rassat, A. Bull Soc Chim Fr 1961, 743.

[8] Onaka, K.; Shinoda, T.; Izumi, Y.; Nolen, E. Chem Lett 1993, 117.