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SYNTHESIS OF 1,3,5-TRIOXANES: A NEW, SIMPLE METHOD USING A BENTONITIC EARTH AS CATALYST‡

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Abstract. *A simple method for synthesizing aliphatic as well as aromatic 1,3,5-trioxanes using as catalyst a bentonitic earth is reported. The yields ranged from good to excellent.*

1,3,5-trioxanes are widely used compounds due to their versatility in different fields: as burning regulators in fumigants for potato tuber sprouting inhibition,[1] as constituents of a stabilizing solution in color photography,[2] as a means of achieving separation of aldehydes from ketones of similar boiling points[3] and in polymer chemistry[4] among others.

The common methods for the synthesis of 1,3,5-trioxanes involve heating and/or use of acidic catalysts such as organic and mineral acids,[5] heteropoly acids,[6] Lewis acids,[7] oxides,[8] ionic exchange resins[9] and electrochemical methods.[10]

We have shown that a Mexican bentonitic earth has unique properties as acidic catalyst in oxidation processes under the influence of infrared or microwave irradiation.[11]

In this paper, we report the use of a commercial bentonitic earth[12] as catalyst for the efficient cyclotrimerization of aldehydes.

The reaction depicted in Scheme I was carried out for isobutyraldehyde, butyraldehyde, isovaleraldehyde and 2-methyl-3(p-*tert*-butylphenyl)propionaldehyde; the bentonitic earth was previously activated by infrared irradiation under low pressure for 4.0 hours and stored in an oven at 150° until use. The reaction times and yields are shown in Table I.

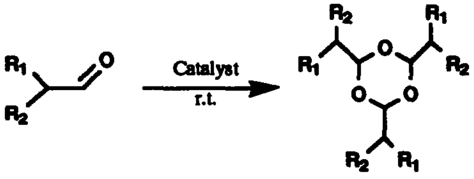


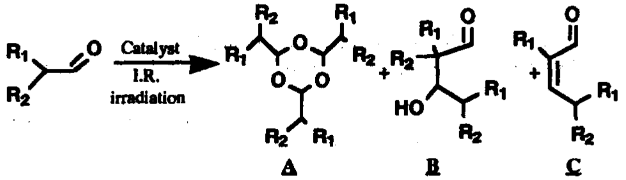
Table I

Compound	R_1	R_2	Time (h)	Yield (%)
1	Me	Me	0.5	90
2	H	Et	8.0	70
3	H	iPr	7.0	60
4	Me	p-$tBuC_6H_4CH_2$	24.0	58

Scheme I

In a typical reaction, 1.0 g of aldehyde was mixed with 0.5 g of the activated bentonitic earth and stirred at room temperature. The conversion was monitored by GC. The reaction mixture was extracted with 20 ml of ethylacetate and filtered over celite; this procedure was repeated four times and the filtrate concentrated under reduced pressure. The residue was purified by column chromatography, preparative TLC or recrystallization.

It is of interest to point out that the same reaction under infrared irradiation produced a mixture of compounds (the corresponding trioxane, the aldol, and the dehydrated product thereof, see Scheme II) for isobutyraldehyde, butyraldehyde and isovaleraldehyde. 2-Methyl-3(p-*tert*-butylphenyl)propionaldehyde gave a complex mixture of uncharacterized products.



R_1	R_2	Time (min)	Yield (%) A	B	C
Me	Me	120	21	12	-
Et	H	120	-	-	80
i-Pr	H	45	14	24	38

Scheme II

These experiments lead us to conclude that the catalyzed reaction with bentonitic earth is a convenient method for the production of 1,3,5-trioxanes.

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References.

1. Dimun, M.; Zeman, S.; Balog, K.; Kosik, S.; Blaha, J.; Koutnik, J.; Hernik, F.; Kabatova, V.; Truchlik, S.; Czech. CS. 269,554 **1991**; Chem. Abstr.; **1992**, 116, p53676v.
2. Ishikawa, M.; Kagawa, N.; Hagiwara, M.; Koboshi, S.; Jpn. Kokai Tokkyo Koho JP 04 24,634 [92 24,634] **1992**; Chem. Abstr.; **1992**, 116, P265477f.
3. Hsu, W. L.; U.S. 4,701,561 **1987**.
4. Yamamoto, S.; Usui, A.; Japan Kokai Tokkyo Koho JP 04 65, 412 [92 65, 412] **1992**, Chem. Abstr.; **1992**, 117, 8760c. Makabe, Y.; Yamamoto, Y.; Jpn. Kokai Tokkyo Koho JP 04 65,413. **1992**. Chem. Abstr.; **1992**, 117, 70575z.
5. Ogorodnikov, A.L.; Katsnel'son, M.G. Neftekhimaya **1990**, 30(6), 830; Chem. Abstr.; **1991**, 115, 113845r.
6. Sato, S.; Sakurai, C.; J. Chem. Soc., Chem. Commun. **1991**, 19, 1327.
7. Yamamoto, N.; Yamashita, I. Osaka Kogyo Gijutsu Shikensho Kiho **1973**, 24(1), 52; Chem. Abstr.; **1973**, 79, 105614n.
8. Krasnov,U.L.; Ozherel'eva, N.K. Obshch. Khim. **1983**, 53(10), 2367; Chem. Abstr.; **1984**, 100, 33909q.
9. Long, C.Y.Shiyou Huangong **1990**, 19(4), 214; Chem. Abstr.; **1991**, 114, 7646w. Liu, H.; Li, L. Huaxue Shijie **1982**, 23(2), 41; Chem. Abstr.; **1984**, 100, 70285d. Shau, S.P.;Sonume,K.K. Chem. Ind. Rev. **1978**,12(3),11; Shadrin, L.P.Rumyantsev Prom-st. Somt. Kauch. **1976**, 9, 9; Chem. Abstr.; **1977**, 86, 89116p. Becker, B.F.; Fritz, H.P.Chem. Ber. **1975**, 108 3292.
10. Becker, B.F.; Fritz, H.P.Chem. Ber. **1975**, 108 3292.
11. García, O.; Delgado,F.; Cano, A.C.; Alvarez, C. Tetrahedron Letters, **1991**, 34, 623. Delgado, F.; Cano, A.C;. García, O.; Alvarado, J.; Velasco, L.;. Alvarez, C.; Rudler, H. Synthetic Commun. **1992**, 22, 2125. Alvarez, C; Delgado, F.; García, O.; Medina ,S.; Márquez, C. Synthetic Commun. **1991**, 21, 619. Delgado, F.; Alvarez, C.; García, O.; Penieres, G.; Márquez,C. Synthetic Commun. **1991**, 21, 2137.
12. Salmón, M.; Angeles, E.; Miranda, R.J. Chem. Soc., Chem. Commun., **1990**, 1188.

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