



Comparison of Several Heterogeneous Catalysts in the Epoxidation of α -Isophorone with Hydroperoxides

J. M. Fraile^a, José I. García^a, José A. Mayoral^{a*}, and François Figueras^b,

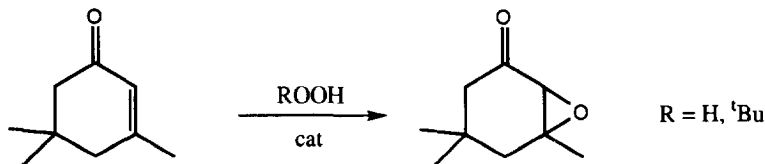
^aDepartamento de Química Orgánica. Instituto de Ciencia de Materiales de Aragón. C.S.I.C.–Universidad de Zaragoza. Facultad de Ciencias. E-50009 Zaragoza (España)

^bInstitut de Recherches sur la Catalyse. 2, Avenue Albert Einstein. 69626 Villeurbanne Cedex (France)

Abstract: Three different methods of epoxidation using heterogeneous catalysts are compared, under different conditions, in the benchmark epoxidation of α -isophorone. The use of *tert*-butyl hydroperoxide/KF-Al₂O₃ in toluene leads to the highest (almost quantitative) yield, whereas the system H₂O₂/hydrotalcite leads to the best result described to date using this oxidant.

Copyright © 1996 Elsevier Science Ltd

Epoxidation of α,β -unsaturated carbonyl compounds is of great interest in organic synthesis, given the usefulness of the epoxides as synthetic intermediates.¹ The classic epoxidation reactions, using hydrogen peroxide in a basic medium, suffer some drawbacks, so that several new methods, such as the use of sodium hypochlorite,² dioxiranes,³ or sodium perborate under phase transfer conditions⁴ have been developed. Recently, *tert*-butyl hydroperoxide (TBHP) has been used in the presence of a titania-silica catalyst,⁵ or KF/Al₂O₃.⁶ On the other hand hydrogen peroxide has also been used as an oxidant in the presence of hydrotalcite.⁷ The use of heterogeneous catalysts has clear advantages relating to the separation and purification of the products, so that improving their performance constitutes an interesting goal. In this communication we will describe the results obtained with three heterogeneous systems in the benchmark reaction of epoxidation of α -isophorone. The reason for choosing this compound is that it is not particularly easy to epoxidise, because the carbon-carbon double bond is β -substituted, leading to a better understanding of the performance of the epoxidation system.



The results obtained using H₂O₂-hydrotalcite (Table) are limited by the low selectivity in the oxidant. Although this selectivity can be improved using an excess of isophorone, in general, it is preferable to work with an excess of oxidant. With TBHP-KF/Al₂O₃ the selectivity in the oxidant is higher, and it is further improved by using an excess of isophorone. Again, the best result is obtained with an excess of oxidant, leading to conversions of up to 96%, which are as good as those described using methyl/trifluoromethyl)dioxirane.^{3a} It

has recently been reported that TBHP–KF/Al₂O₃ is unable to epoxidise α -isophorone;⁶ however, in our work, using this system leads to the best results described to date for this reaction. Although the catalyst used is not exactly the same, this does not justify such a huge difference of behaviour, and we believe that the reason for this change is the use of toluene instead of acetonitrile—which is acid enough to react with the catalyst—as the reaction medium. This dramatic change reveals the active role that the solvent may play in these systems.

It is important to note that H₂O₂ cannot be used with KF/Al₂O₃ because of the solubility of KF, but hydrocalcite is not basic enough to promote the epoxidation with TBHP.

Table. Results obtained in the epoxidation of α -isophorone with several systems.^a

Oxidant/catalyst	isophorone (mmol reagent·g ⁻¹ cat.)	oxidant	solvent	T (°C)	t (h)	%epoxide	%select. in oxidant
TBHP–Ti/SiO ₂ ^b	154	27	toluene	60	24	30	53
	27	27	toluene	20	48	3	21
	4	18	toluene	60	24	20	12
H ₂ O ₂ –Hydrocalcite ^c	154	27	methanol	60	24	41	41
	127	27	methanol	20	24	11	39
	6.6	24.6	methanol	20	72	66	18
TBHP–KF/Al ₂ O ₃ ^d	154	27	toluene	60	1	45	82
	154	27	toluene	60	24	55	83
	27	27	toluene	20	24	30	69
	4	18	toluene	20	24	96 ^e	59
	6	18	toluene	20	24	84	60

^a Reactions are monitored by GC, the catalyst is separated by filtration, washed, and the product purified by flash chromatography on silica gel, using CH₂Cl₂ as an eluent, and identified by ¹H-NMR (ref. 3b). ^b Obtained by treating silica gel with Ti(OⁱPr)₄ (ref. 8). ^c Mg/Al = 2.8. ^d Purchased from Fluka, it contains 5.5 mmol of fluoride per gram of solid. ^e 82% isolated yield.

Acknowledgements: This work was made possible by the generous financial support of the Comisión Interministerial de Ciencia y Tecnología (Projects MAT93-0224 and MAT96-1053). We are also indebted to the E.U. (Contract INTAS 93-1159).

REFERENCES

- (a) Gozinsky Smith, J.; *Synthesis*, **1984**, 629. (b) Rao, A. S.; Paknikar, S. K.; Kirtane, J. G.; *Tetrahedron*, **1983**, *39*, 2323. (c) Parker, R. E.; Isaacs, N. S.; *Chem. Rev.*, **1959**, *59*, 737. (d) Alcaraz, L.; Harnett, J. J.; Maskowski, C.; Martel, J. P.; Gall, T. L.; Shin, D.-S.; Falck, J. R.; *Tetrahedron Lett.*, **1994**, *35*, 5449, and references cited therein.
- Foucaud, A.; Bakouetila, M.; *Synthesis*, **1987**, 854, and references cited therein.
- (a) Yang, D.; Wong, M.-K.; Yip, Y.-C.; *J. Org. Chem.*, **1995**, *60*, 3887. (b) Murray, R. W.; Singh, M.; Jeyasaman, R.; *J. Am. Chem. Soc.*, **1992**, *114*, 1346.
- Straub, T. S.; *Tetrahedron Lett.*, **1995**, *36*, 663.
- Hutter, R.; Mallat, T.; Baiker, A.; *J. Catal.*, **1995**, *157*, 665.
- (a) Vadav, V. K.; Kapoor, K. K.; *Tetrahedron*, **1996**, *52*, 3659. (b) Vadav, V. K.; Kapoor, K. K.; *Tetrahedron Lett.*, **1994**, *35*, 9481.
- Cativiela, C.; Figueras, F.; Fraile, J. M.; García, J. I.; Mayoral, J. A.; *Tetrahedron Lett.*, **1995**, *36*, 4125.
- (a) Fraile, J. M.; García, J. I.; Mayoral, J. A.; de Mènorval, L. C.; Rachdi, F.; *J. Chem. Soc., Chem. Commun.*, **1995**, 539. (b) Cativiela, C.; Fraile, J. M.; García, J. I.; Mayoral, J. A.; *J. Mol. Catal. A*, in the press.

(Received in UK 6 May 1996; revised 25 June 1996; accepted 28 June 1996)