Pergamon

Tetrahedron Letters, Vol. 38, No. 22, pp. 3857-3860, 1997

0040-4039/97 $17.00 + 0.00

PII: S0040-4039(97)00771-5

MAGTRIEVE™ AN EFFICIENT, MAGNETICALLY RETRIEVABLE and RECYCLABLE OXIDANT

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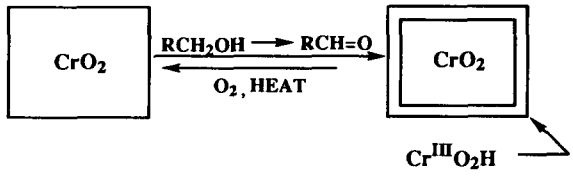
Key Words: chromium dioxide, manganese dioxide , oxidation, alcohols, aldehydes, ketones

ABSTRACT: Magtrieve™ is a mild and selective oxidant for a variety of alcohols and, in addition to being magnetically retrievable, is superior to activated MnO_2 in most cases - particularly for less active alcohols such as simple alkanes. © 1997 Elsevier Science Ltd.

While a myriad of methods exist for oxidations in synthetic organic chemistry, there remains a need for selective oxidants whose reduction byproducts can be easily separated and do not stress the environment.[1] Magtrieve™ is DuPont's trademark for its magnetically retrievable oxidant based on tetravalent chromium dioxide (CrO_2).[2] The chemistry of CrO_2 has not been extensively explored in organic chemistry, largely because the material as commercially produced is passivated towards reaction with organic materials by a reductive surface treatment[3] for application in magnetic tape. Magtrieve™ is CrO_2 produced in the commercial process[4] for making magnetic tape pigment but isolated prior to the reductive surface treatment. We describe here our preliminary work that shows that Magtrieve™ is a selective, heterogeneous oxidizing agent, whose reduced form stays on the CrO_2 crystal surface. Since only the surface of the CrO_2 is reduced, it is still ferromagnetic and can be readily removed by simple magnetic separation.

Reactivity is comparable to activated manganese dioxide[5], but in many cases the yields are higher, the reactions are cleaner and the work-up dramatically simpler with Magrieve™. The reduced trivalent chromium oxyhydroxide surface can be reconverted to CrO_2 by heating in air at 300-350 deg. C., for 1-2 hrs. thus providing an avenue for recyclability and cost-effectiveness. As indicated in the table, for geraniol oxidation, the reaction proceeds as effectively after the 3rd recycling as with fresh Magtrieve™ .



Magtrieve™ is characterized as dense (Sp. Gr. 4.86 g./cc.), acicular (typically 0.3 microns long by 0.03 microns in diameter) crystals with a specific surface area of 30 m^2/g[7]. It is a strong ferromagnet with a typical coercivity of 600 Oersteds and a specific magnetization of 80 emu/g.[7] These magnetic properties allow it to be easily retrieved by a common permanent magnet with a magnetic strength of a few thousand gauss.

Oxidation of alcohols with CrO_2. Typical procedure.

A 100-ml round-bottomed flask equipped with a water cooled condenser and a 25 mm mechanically rotated Teflon® paddle was charged with a slurry of 10.0 g of Magtrieve™ and 1.00 g of geraniol (Aldrich Chemical Company; catalog number 16,333-3/98%) in 25 ml of chloroform[a]. After refluxing for 4 hours with mechanical stirring the slurry was cooled to room temperature and a horseshoe magnet (2 in. across and 3/8 in. thick; ca. 2000-5000 gauss) was placed on one side of the flask and the liquid was decanted off. The chromium solids were rinsed three times with 15 ml portions of chloroform which were combined with the original decantate[b]. The solvent was removed using a rotatory evaporator giving 0.90 g of clear liquid residue. The proton NMR and IR of this material indicated complete conversion to citral as a mixture of geranial and neral in the same ratio (95:5) as the starting geraniol/nerol alcohol mixture.

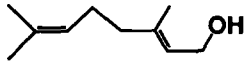
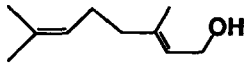
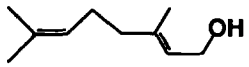
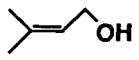
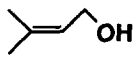
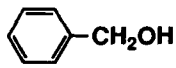
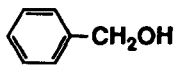
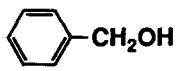
Recycling of the Magtrieve™ typically involved heating in a muffle oven with a 15 standard cubic feet per hour air purge at 325°C for 2 hrs.

[a]Only the surface of the Magtrieve™ is reduced, so like MnO_2, an excess is required.

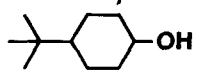
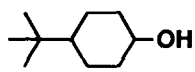
[b]Although magnetic retrieval is, in general clean and efficient, we sometimes also filter the crude reaction mixtures through a thin bed of Celite™ to insure the absence of traces of Magtrieve™ which would of course interfere with analysis by NMR.

Table I summarizes the oxidation of a variety of alcohols with Magtrieve™ and with activated MnO2. The selectivity of Magtrieve™ is demonstrated in the smooth conversions of the unsaturated activated alcohols (geraniol, isopentenol, benzyl alcohol) to the corresponding aldehydes in excellent isolated yields without overoxidation. As demonstrated in one of the geraniol oxidations, the yield is still excellent in a fourth oxidation using Magtrieve™ after its third regeneration by heating in air. As determined with a benzyl alcohol reaction, the amount of residual chromium in the isolated product is quite low. Surpisingly, we find that Magtrieve™ also smoothly converts a saturated primary alcohol, decanol, to the corresponding aldehyde in excellent isolated yield without overoxidation to the acid. In most of the comparisons shown with activated MnO2, Magtrieve™ gives predominantly the same products but with better conversions and better isolated yields. In the reaction with decanol, however, Magtrieve™ gives essentially complete conversion under conditions where only slight conversion occurs with activated MnO2. In the comparisons with a saturated secondary alcohol, t-butylcyclohexanol, both Magtrieve™ and activated MnO2 give significantly less conversion under conditions where the activated alcohols react completely. However, as in the case of the primary saturated alcohol, Magtrieve™ appears more reactive than activated MnO2 towards the unactivated alcohol. In all of the comparisons, recovery is routinely poorer for the activated MnO2 reactions..

Table 1 Oxidation of alcohols with Magtrieve™ and activated MnO_2

SUBSTRATE	PRODUCT	OXIDANT	SOLVENT	HOURS AT REFLUX	ISOLATED YIELD %
	citral	Magtrieve™	$CHCl_3$	4	90[a]
	citral	MnO_2[b]	$CHCl_3$	5	77[a]
	citral (after the 3rd regeneration)	Magtrieve™	$CHCl_3$	3	90[a]
	isopentenal	Magtrieve™	CH_2Cl_2	4	90
	isopentenal	MnO_2	CH_2Cl_2	4 (+ unreacted s. material)	70
	benzaldehyde	Magtrieve™	CH_2Cl_2	2	95[c]
	benzaldehyde	MnO_2	CH_2Cl_2	3 (+ unreacted s. material)	60
	benzaldehyde	Magtrieve™	toluene	1	95
	decanal	Magtrieve™	toluene	5.5	95
	decanal	MnO_2	toluene	5.5 (+ unreacted s. material)	<10

For comparison only - under identical conditions, work up; not optimized:

	4-t-butylcyclohexanone	Magtrieve™	toluene	6 (95% recovered, remainder unreacted s. material by NMR/IR)	61
	4-t-butylcyclohexanone	MnO_2	toluene	6 (25% recovered, remainder unreacted s. material)	<10

(a) Complete conversion of geraniol/nerol with same ratio of 95:5
(b) Aldrich Chemical Co., product number 21467-6
(c) Inductively coupled plasma analysis indicated < 12 ppm residual chromium

In summary, we believe that Magtrieve™ offers significant potential as a mild, selective oxidant with freedom from environmental problems resulting from its strikingly simple work-up. For lab-scale syntheses it should be preferred over activated MnO_2, especially for simple saturated, primary alcohols (decanol example in the Table). It should likewise be preferred over the numerous examples of specially prepared heterogeneous oxidants including those supported on alumina, silica, and clay[8], on resins[9] and on carbon[10], again due to good activity, availability and easy magnetic retrieval. Work continues to better understand the scope of these reactions and drive cost effectiveness through higher surface area Magtrieve™ and recyclable processes.

References and Notes

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(*Received in USA* 31 *March* 1997; *accepted* 17 *April* 1997)