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EXCLUSIVE 1-4 REDUCTION OF CONJUGATED KETONES BY SODIUM DITHIONITE

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Abstract : α -β unsaturated aldehyde and ketones were exclusively reduced to the corresponding saturated aldehyde and ketones by the use of sodium dithionite under phase- transfer catalysis conditions. Neither allylic nor saturated alcohols are formed.

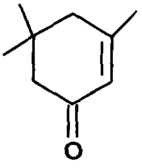
Sodium dithionite is an inexpensive and readily available reducing agent with commercial importance in textile industry as a bleaching agent and vat dyeing reductant. Its redox potential (-1.12 V) is close to that of sodium borohydride (-1.24 V) (1) so it could be an interesting substitute if, as well as its relatively low cost (2), it could lead to similar or more selective reductions.

In the past, various nitrogenous functionalities such as nitro and azo compounds, oximes and imines have been reduced to amino derivatives by using sodium dithionite (3) ; however its lack of solubility in organic media thwarted a broader use in organic chemistry. Recently, the use of polar solvents (4) or phase-transfer catalysis (5) allowed the reductions of carbonyls and dienoic esters respectively.

In this work, we were interested in the competitive 1-4 vs. 1-2 reduction of conjugated enones ; isophorone 1 was first examined under the condition of phase-transfer catalysis with various base and quaternary ammonium salts (Table).

3,3,5-trimethyl cyclohexanone appeared as the sole reduction product with no trace of either allylic or saturated alcohol being detected.

This exceptionnal selectivity thus found was then checked on various α -β unsaturated monoterpenic aldehyde and ketones (2-5), following the procedure described for 1 the sole products also are the saturated species resulting from the exclusive reduction of the C=C double bound conjugated to the carbonyl ; no detectable trace of alcohols were found (Table).



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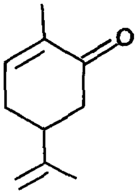

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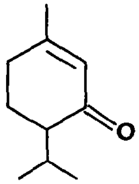

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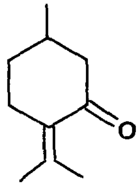

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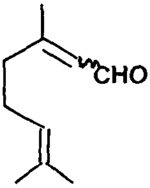

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Table : Reduction[a] of isophorone and monoterpenic aldehyde and ketones with sodium dithionite.

Substrate	Products[b]	Yield%[c] (time-h)	Selectivity %
isophorone 1	trimethylcyclohexanone	84 (2)	100
carvone 2	dihydrocarvone	82 (0.5)	100
piperitone 3	menthone[d]	54 (2)	100
pulegone 4	menthone[e]	74 (2.5)	100
citral[f] 5	citronellal	69 (1.5)	100

a) under nitrogen atmosphere at 80°C in a water-benzene mixture, molar ratio of Aliquat®/$NaHCO_3$/$Na_2S_2O_4$/ substrate 0.3/18/9/1
b) products compared with commercially available authentic samples or obtained by hydrogenation with Pd/C.
c) reduction monitored by GLC.
d) menthone/isomenthone 59/41
e) menthone/isomenthone 57/43
f) mixture of geranial and neral

Good selectivities in the 1-4 reduction of conjugated enones have been found with borohydride associated with cryptands or ammonium species (6) ; the highest selectivities reported until now required the use of complex Li-Cu hydrides (which are not easy to prepare or to handle) (7) or the use of iron carbonyls (8) with prolongated heating time.

In the example chosen here as typical of conjugated enones, sodium dithionite demonstrated its superiority as selective reducing agent considering the ease of work-up and availaibility.

References and notes

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