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SELECTIVE CATALYTIC HYDROGENATIONS
WITH CHROMIUM-PROMOTED RANEY NICKEL

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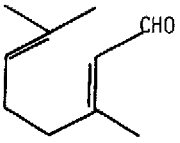
Although viewed as a difficult problem[1], selective catalytic hydrogenations of unsaturated aldehydes to unsaturated alcohols have been achieved in several instances using a variety of catalytic systems and are well reported[2]. In unpublished work done a few years ago[3], we hydrogenated citral (1) and citronellal (2) to citronellol (3) using a chromium-promoted Raney nickel catalyst in the presence of methanol. Citronellol is produced in 94% yield in 2 to 6 hours at 75^0 and about 45 psi of hydrogen.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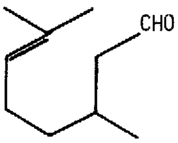
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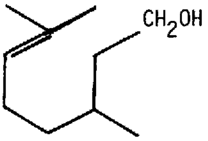
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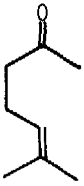
However, catalytic hydrogenation of unsaturated aliphatic ketones proceed normally with preferential saturation of the olefinic group[4]. There appear to be very few exceptions. One is an α,β-unsaturated ketone $Ph\cdot CH{=}CH\cdot CO\cdot CH_3$ that is hydrogenated to $Ph\cdot CH{=}CH\cdot CH(OH)CH_3$ in the presence of colloidal Pd and promoters[5]. Another example is the tetra-substituted olefinic ketone (4), which is converted to the corresponding unsaturated carbinol with platinum oxide in ethanol[6].

We have now achieved preferential reduction of the keto group in 5, 6, 7, 8 and 9 and, thus, have obtained the corresponding unsaturated alcohols using chromium-promoted Raney nickel catalyst in the presence of a strong inorganic base and methanol.

The catalytic system is quite specific. Substitution of the chromium-promoted Raney nickel by any other metal catalyst commonly used in catalytic hydrogenations, or omission of the base or of the methanol, result in non-selectivity. Alcohols other than methanol and to some degree of ethanol are ineffective.



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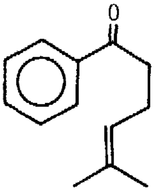

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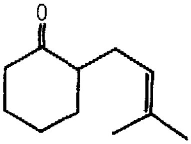

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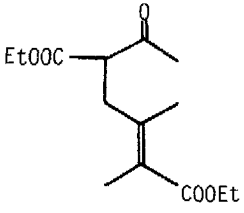

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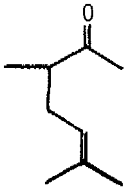

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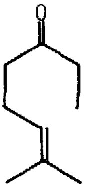

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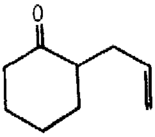
The hydrogenations are carried out at room temperature and moderate pressures of about 40 psi of hydrogen. Depending on the ketone and the degree of desired completion, the time can vary from one to several hours. The reaction rate is increased by the presence of *small amounts of water and an amine. Interestingly, there is an optimum amount of water below* or above which the rate is reduced.

The typical recommended conditions for one mole of unsaturated ketone are as follows: 4.0g chromium-promoted Raney nickel[7] in suspension with about an equal amount of water, 60g of methanol, 5g triethylamine and 4.5g of 10% solution of KOH or KOMe in methanol.

Results are summarized in the following table.

However, in several unsaturated ketones seemingly related to those in the Table, hydrogenation proceeds preferentially on the olefinic moiety.



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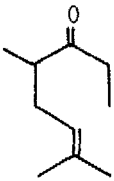

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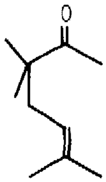

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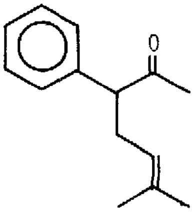

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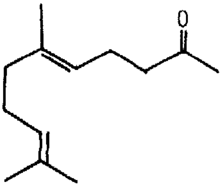

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Monosubstituted olefinic groups as in 2-allylcyclohexanone (10) are hydrogenated first. The influence of the steric encumbrance at the carbons adjacent to the carbonyl group in 11, 12

Ex. #	Ketone	Reaction Time/Hrs.	% of Components after Hydrogenation[a]			
			Original Ketone	Unsaturated Alcohol	Saturated Ketone	Saturated Alcohol
1	5	2.2	3.8	88.5	.8	4.4
		16	0.3	82.5	--	15.4
2	6	2.1	21.9	72.8	0.7	1.5
3	7	7	26.6	69.4	2.7	--
		24	4.7	89.3	2.8	1.6
4	8 + 9[b]	1.5	56.9	41.4	1.7	--
		3	31.1	65.2	2.8	0.9
		4.5	16	78.7	2.4	2.9
		7.5	4.1	88	1.8	6.1
5[c]	"	6.5	69.4	28.7	1.8	--
6[d]	"	7.0	97.6	--	1.8	--
7[e]	"	21.0	95.4	1.9	0.9	--
8[f]	"	7	58.0	36.1	4.1	--
9[g]	"	4.5	84.2	12.2	1.3	--
		21.0	47.3	46.4	4.0	0.9

(a) Determined by glc using pure standards. (b) Mixture 85% isomer 8 + 15% 9. (c) Amine omitted. (d) Methanol reduced to 4 ml/mole. (e) *n*-Propyl alcohol 70 ml used instead of MeOH; similar results with *t*-BuOH, isopropanol, THF or benzene. (f) Water omitted. (g) 15g/mole Water instead of the 5g/mole normally used.

and 13 and of the shielding exercised by the configuration of the C_{11}-chain in 14 was evidenced by reduced rate of hydrogen addition and loss of selectivity. Also, α,β-unsaturated ketones such as mesityl oxide have their olefinic groups hydrogenated first.

REFERENCES AND FOOTNOTES

(1) Chemtech, June 1975, p. 382.

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(4) P. N. Rylander, "Catalytic Hydrogenation over Platinum Metals," page 271, Academic Press, N.Y., (1967).

(5) Z. Csuros, K. Zech, and I. Géczy, Hung. Acta Chim., 1, 1 (1946).

(6) R. Adams and M. Gianturco, J. Am. Chem. Soc., 79, 169 (1957).

(7) Typical among others commercially available is W. R. Grace & Co. Raney #24 - digested, ready for use.