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HETEROGENEOUS DEOXYGENATION OF KETONES[1]

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Summary: Relatively unhindered ketones are converted directly to the corresponding hydrocarbons in the presence of hydrogen at normal pressures and a Ni/Al_2O_3 catalyst in a simple gas-phase reactor.

Transformations of carbonyl groups to the corresponding methylene derivatives is an important operation in organic synthesis. Since Wolff-Kishner reduction requires long reaction times for unactivated ketones,[2a] improved variations have been developed involving hydrogenation with metal hydrides.[2b] Thus, tosylhydrazones can be cleaved selectively under mild conditions by $NaBH_3CN$ or catechol borane in moderate to good yields.[3,4] In another two-step reaction, ketones are converted to selenoacetals and reduced.[5] These and other multi-step reaction sequences for the deoxygenation of carbonyl groups suffer from the considerable experimental effort required. The standard direct method, Clemmensen reduction, can be applied successfully to aromatic aldehydes and ketones, but unactivated aliphatic carbonyl compounds require long reaction times and yields are often low.[2c] A more recent one-step process employs triethylsilan in combination with trifluoroborane.[6] Catalytic reduction via hydrogen transfer, which has only been reported for aromatic ketones and aldehydes, is achieved by the use of cyclohexene and a Pd/C catalyst.[7] The development of simple methods for the deoxygenation of both unactivated and activated carbonyl groups is still a challenge for the synthetic organic chemist.

Deoxygenation of ketones with hydrogen (e.g., eq 1) is thermodynamically favorable.[8] This stresses the potential application of catalytic methods.

$$CH_3COCH_3 + 2H_2 \longrightarrow CH_3CH_2CH_3 + H_2O \qquad \Delta G_R^{\circ}\ (298^{\circ}\ K) = -23.9\ \text{kcal/mol} \quad (1)$$
$$(500^{\circ}\ K) = -18.9\ \text{kcal/mol}$$

Such reactions, in principle, might proceed in two stages, reduction of ketone to alcohol (eq 2) and reduction of alcohol to hydrocarbon (eq 3). It is important to realize that the first stage becomes thermodynamically unfavorable at higher temperatures, but the second stage is nearly independent of temperature and provides the driving force for the overall process.

$$CH_3COCH_3 + H_2 \longrightarrow CH_3CHOHCH_3 \qquad \Delta G_R^{\circ}\ (298^{\circ}\ K) = -5.9\ \text{kcal/mol} \quad (2)$$
$$(500^{\circ}\ K) = +0.8\ \text{kcal/mol}$$

$$CH_3CHOHCH_3 \quad + \quad H_2 \longrightarrow \quad CH_3CH_2CH_3 \qquad \Delta G_R^{\circ}\ (298^{\circ}\ K) = -18.0\ kcal/mol \quad (3)$$
$$(500^{\circ}\ K) = -19.7\ kcal/mol$$

Indeed, we reported the high yield transformation of adamantanone into adamantane by hydrogenation in the presence of a nickel-alumina catalyst at 520° K.[1c] This gas phase procedure with an optimized Ni catalyst[10] has now been extended to a representative collection of ketones (see Table). The method appears to be effective for relatively unhindered ketones. The major drawback is the lack of selectivity. Other functional groups are lost under the same conditions.[1c]

Linear and cyclic ketones are deoxygenated in high yield as are some polycyclic ketones. The exceptions, 2-norbornanone and 2-bicyclo[3.2.1]octanone, did not react at all, even though camphor was reduced. Whereas cyclopentanol gave high yields of cyclopentane,[9] cyclopentanone gave the poorest result among the monocyclic ketones. The strained 4-protoadamantanone only suffered partial rearrangement (to adamantane) under the reaction conditions; the same was true for camphor. Steric hindrance seems to be important (as expected for such a surface reaction). This was demonstrated by the recovery of increasing amounts of the starting ketones, 3,3-dimethyl-2-butanone and the methylated 3-pentanones (Table), after reaction. Since the hydrogenolysis of alcohols with Ni-catalysts was not as sensitive to steric hindrance,[9] such encumbered ketones must be converted to alcohols separately before hydrogenolysis to the hydrocarbon can be carried out successfully. In agreement with the thermodynamics (eqs 2 and 3), the corresponding alcohols are reduced to hydrocarbons under much milder conditions than the ketones.[9] Evidence for the intermediacy of alcohols is provided by the wellknown reduction of ketones to alcohols by Raney-nickel.[11] However, alcohols were not detected under the conditions of the present experiments.

Mechanistic studies using deuterium as a carrier gas were unsuccessful; H/D-exchange occurred statistically at lower temperatures where the carbonyl groups were not attacked.

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10) Catalyst Preparation: 5.5 g $Ni(NO_3)_2 \cdot 6H_2O$, dissolved in 20 ml water, was stirred with 10g alumina (Woelm W200, neutral) and the water was evaporated on a rotary evaporator. The residue was dried at 120°C for 5 hours. A portion, 5 g, of this catalyst was ground finely and packed between glass wool plugs in the center of the reaction tube (Ø 25 mm). The reduction of the catalyst was performed in a slow stream of hydrogen (30 ml/min) at atmospheric pressure starting with one hour reaction time at 100°C. The temperature was raised stepwise by 50°C (each temperature being maintained for one hour); the final temperature was 400°C. The catalyst must be reactivated at 400°C for 30 min after each experiment, but then can be used repeatedly. The flow apparatus used and the reaction procedure has been described previously.[1d]

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Table: Gas Phase deoxygenation of ketones in the presence of H_2 and a Ni/Al_2O_3 catalyst[a]

Compound	Product	Yield	Recovered Educt
2-hexanone	hexane	88%	
4-heptanone	heptane	88%	
5-nonanone	nonane	81%	
cyclopentanone	cyclopentane	24%	
cyclohexanone	cyclohexane	90%	
cycloheptanone	cycloheptane	95%	
cyclooctanone	cyclooctane	91%	
2-adamantanone	adamantane	92%	
4-protoadamantanone	protoadamantane: adamantane (4:6)	87%	
camphor	camphane: iso-camphane[c] (6:4)	91%	
3,3-dimethyl-2-butanone	3,3-dimethylbutane	46%	20%
2,4-dimethyl-3-pentanone	2,4-dimethylpentane	25%	62%
2,2,4,4-tetramethyl-3-pentanone	not identified		70%
2-norbornanone	no reaction		100%
2-bicyclo[3.2.1]octanone	no reaction		100%

[a] Conditions: 190°C, 25 ml/min H_2-flow; catalyst, see footnote 10. [b] Products identified by glc comparison with authentic samples. [c] The exo-endo ratio was not determined.

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