Amberlyst 15, a Superior, Mild, and Selective Catalyst for Carbonyl Regeneration from Nitrogeneous Derivatives

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Various tosylhydrazones, oximes, 2,4-dinitrophenylhydrazones, and semicarbazones were converted into the corresponding carbonyl compounds, mostly in quantitative yields, *via* equilibrium exchange with aqueous acetone, by use of Amberlyst 15 as acidic catalyst. Good results were obtained also with aldehyde derivatives. Groups which are acid-sensitive survive under these reaction conditions.

Regeneration of the carbonyl group from its derivatives under mild conditions is an important process in synthetic organic chemistry. Hydrazones and oximes are employed as ketone and aldehyde functional group equivalents in synthesis, both because they provide convenient protection for the carbonyl group and because they are important synthetic intermediates.[1] There has therefore been considerable interest in the development of mild techniques for the conversion of oximes,[2–5] hydrazones,[6–10] and tosylhydrazones back into carbonyl compounds.[11–16] Most of the reported methods require strongly oxidative or reducing, acidic or basic media, or tedious procedures and/or expensive reagents. Regeneration of carbonyl compounds *via* equilibrium exchange, by use of acetone with boron trifluoride–ether complex as catalyst, has been reported to be efficient only with tosylhydrazones.[17] Erker *et al.*,[18] have reported the utilization of acetone for regeneration of ketones from various nitrogeneous derivatives, but this method is not applicable to aldehydes, which can be recovered only in very low yields. Furthermore long reaction times are often required.

In connection with our studies on reactions carried out with heterogeneous catalysts,[19] we have found that Amberlyst 15, a macroreticular ion-exchange resin which contains strongly sulphonic groups, is an excellent and far superior catalyst for regeneration of carbonyl compounds from nitrogeneous derivatives (see Table), when acetone is used as exchange reagent.

Our method is carried out at room temperature or 80 °C (see Table) by simply dissolving the appropriate carbonyl derivative (**1**) in acetone–water, with a certain amount of Amberlyst 15 as catalyst, and leaving the mixture for 5—24 h. However, for aldehyde regeneration, it was found convenient to add paraformaldehyde (10 equiv.) also.

Yields are high and work-up is exceedingly simple, only involving removal of solvent, extraction with pentane, filtration, and evaporation, to obtain the product in a high state of purity (at least 97%); no further purification steps are required.

Our procedure is applicable to various nitrogeneous derivatives such as tosylhydrazones, oximes, 2,4-dinitrophenylhydrazones, and semicarbazones. Limited reaction times are

Table. Carbonyl compounds (**2a**—**t**) regenerated from nitrogeneous derivatives (**1a**—**t**)

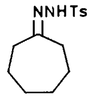
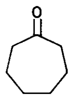
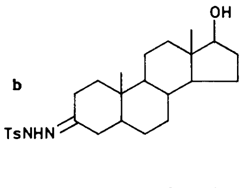
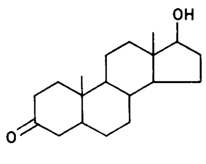
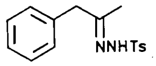
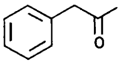
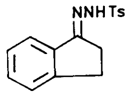
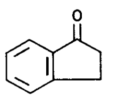
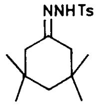
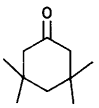
	Derivative (**1**)	Carbonyl compound[a] (**2**)	Yield[b] (%)	Time (h)	Temp. (°C)[c]
a			90	23	R.t.
b			97[d]	22	R.t.
c			91	24	R.t.
d			88	23	80
e			85	21	R.t.

Table (*continued*)

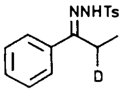
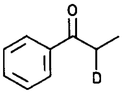
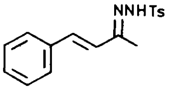
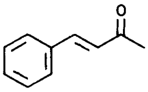
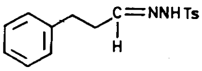
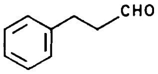
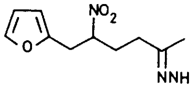
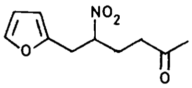
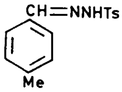
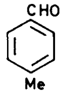
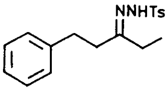
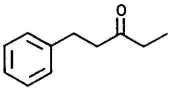
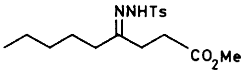
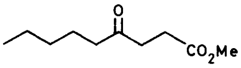
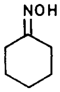
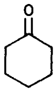
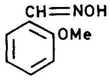
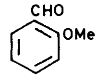
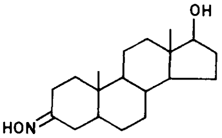
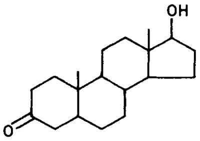
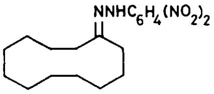
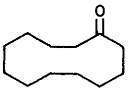
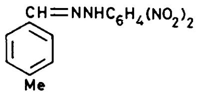
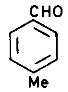
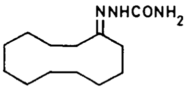
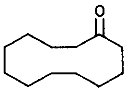
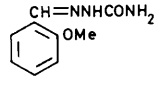
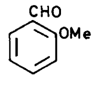
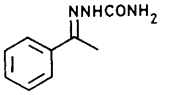
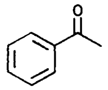
	Derivative (**1**)	Carbonyl compound[a] (**2**)	Yield[b] (%)	Time (h)	Temp. (°C)[c]
f			86	24	R.t.
g			91	22	80
h			90	21	80
i			90	20	R.t.
j			86	24	80
k			93	22	R.t.
l			91	22	R.t.
m			92	21	R.t.
n			88	4	80
o			90[d]	22	R.t.
p			92	5	80
q			61	23	80
r			98	15	80

Table (*continued*)

	Derivative (**1**)	Carbonyl compound[a] (**2**)	Yield[b] (%)	Time (h)	Temp. (°C)[c]
s			85	16	80
t			90	10	80

[a] The carbonyl compounds were compared with authentic samples (m.p., b.p., i.r., and ^{1}H n.m.r.). [b] Yields refer to pure isolated products. [c] R.t. = room temp. [d] Extraction with ether instead of pentane (see Experimental section) gave better results.

necessary; groups which are acid-sensitive such as furyl derivatives, esters, or ethers survive and, above all, excellent results are obtained in aldehyde regeneration. We consider that the combination of Amberlyst 15 with acetone is one of the most convenient of existing methods for carbonyl regeneration from nitrogeneous derivatives, on the basis of its simiplicity and cheapness, and the high yields obtained with a large variety of derivatives, under mild conditions.

Experimental

The starting tosylhydrazones, oximes, 2,4-dinitrophenylhydrazones, and semicarbazones were prepared from the corresponding carbonyl compound by the usual methods.[20,21] M.p.s were determined with a Buchi apparatus. I.r. spectra were recorded with a Perkin-Elmer 257 spectrophotometer. ^{1}H N.m.r. spectra were recorded at 90 MHz with a Varian EM 390 instrument. T.l.c. analysis was performed with hexane–ethyl acetate (8:2); spots were located with u.v. light or with a phosphomolybdic reagent. G.l.c. analyses were performed with a Carlo Erba Fractovap 4160 instrument with an OV1 capillary column. The purity of the isolated compounds was checked by comparison (i.r. and ^{1}H n.m.r. spectra, m.p. or b.p., t.l.c., and g.l.c. analyses) with samples from commercial sources or prepared according to known procedures. Amberlyst 15 was purchased from Carlo Erba, Italy.

Regeneration of Carbonyl Compounds from Tosylhydrazones, Oximes, 2,4-Dinitrophenylhydrazones, and Semicarbazones: General Procedure.—A 250 ml flask, equipped with reflux condenser and magnetic stirrer, was charged with the appropriate nitrogeneous derivative (**1**) (0.01 mol) in acetone–water (10:1; 66 ml) (0.1 mol of paraformaldehyde was added for aldehyde regeneration) and Amberlyst 15 (2 g). Stirring was continued at room temperature or 80 °C for the appropriated time (Table). The progress of the reaction can be conveniently monitored by t.l.c. or g.l.c. The acetone was removed under reduced pressure. Extraction with pentane (3 × 20 ml), filtration, and evaporation gave the pure carbonyl compound (**2**) at least 97% pure.

Acknowledgements

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