Regeneration of Ketones from Hydrazones, Oximes, and Semicarbazones by Benzeneseleninic Anhydride

By Derek H. R. Barton*, David J. Lester, and Steven V. Ley
(*Chemistry Department, Imperial College, London* SW7 2AY)

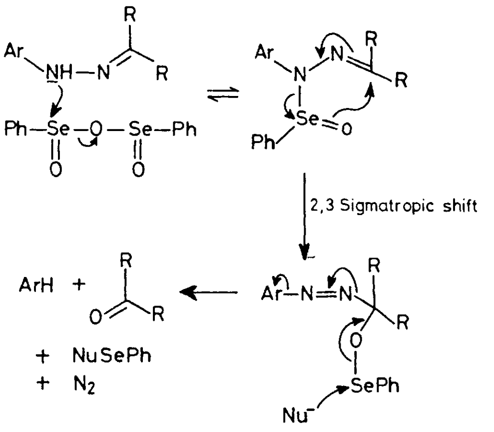
Summary Treatment of ketone hydrazones, oximes, and semicarbazones with benzeneseleninic anhydride readily affords the parent carbonyl compound in good yields, even in cases resistant to known methodology.

TABLE. Conversion of ketone derivatives into the parent ketone with $(PhSeO)_2O$

Derivative	Benzophenone		(1)		(2)		(3)	(4)
	% Yield[a]	Time	% Yield	Time	% Yield	Time	% Yield	% Yield
Phenylhydrazone	90 (81)	3 h	64 (52)	10 h	57 (40)	10 h		
p-Nitrophenylhydrazone	56	3 days	95 (83)	10 h	57 (41)	40 h	86 (73)	96 (43)[b]
2,4-Dinitrophenylhydrazone	N.R.	3 days	25 (8)	24 h	3–5	40 h		
Tosylhydrazone	95 (89)	20 min	97 (87)	20 min	86 (74)	20 min		
Oxime	89 (76)	3 h	83 (60)	50 min	96 (80)	50 min		
Semicarbazone	89 (71)	2 h	83 (67)	4 h	85 (71)	4 h		
NN-Dimethylhydrazone	N.R.	24 h						

[a] Recrystallised yields in parentheses. [b] Isolated as the 1,2α-epoxide

THE conversion of ketonic hydrazones, oximes, and semicarbazones into the parent carbonyl compound under mild conditions is not always easy. We conceived that benzene seleninic anhydride[1] $[(PhSeO)_2O]$ would serve this purpose as in the Scheme.



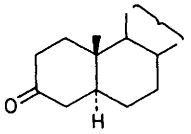
(Nu⁻ = nucleophile, suitably $PhSeO_2^-$)

SCHEME

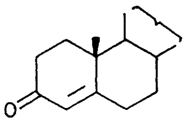
The imino-derivatives (Table) were treated with the anhydride (1·1 mol. equiv.) in dry tetrahydrofuran at 50—60 °C to give ketones in good yield (Table). Selenium dioxide did not act as a smooth oxidant in this reaction and benzeneseleninic acid was without effect.

The rate of removal of the hydrazone group from benzophenone 2,6-dimethylphenylhydrazone was shown to be slower (× 10) than from the corresponding phenylhydrazone. Also *NN*-dimethylhydrazones and *O*-methyl oximes failed to react under our conditions. Removal of the *p*-nitrophenylhydrazone with the anhydride gives nitrobenzene (*ca.* 96%) as one of the by-products.

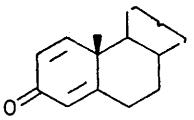
The mechanism in the Scheme accounts for these observations. It is, however, not known whether ionic or radical species are involved in the fragmentation of the intermediate, but we favour the former.



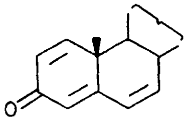
(1)



(2)



(3)



(4)

(all cholesterol derivatives)

This new procedure has advantages over existing methods.[2] For example, we have reported[3] that the anions of the *p*-nitrophenylhydrazones of saturated ketones were dehydrogenated in excellent yield by treatment with nitrobenzene to afford αβ-unsaturated derivatives. We now draw attention (see Table) to the ready conversion of the *p*-nitrophenylhydrazones of cholesta-1,4-dienone (**3**) and -1,4,6-trienone (**4**) (prepared by this electron transfer dehydrogenation) to the corresponding ketones. All other methods for this conversion have proved unsatisfactory.

(*Received, 2nd May* 1977; *Com.* 421.)

[1] D. H. R. Barton, P. D. Magnus, and M. N. Rosenfeld, *J.C.S. Chem. Comm.*, **1975**, 301; D. H. R. Barton, A. G. Brewster, S. V. Ley, and M. N. Rosenfeld, *ibid.*, **1976**, 85; **1977**, 147; D. H. R. Barton, S. V. Ley, P. D. Magnus, and M. N. Rosenfeld, *J.C.S. Perkin I*, **1977**, 567.

[2] For a leading reference see C. A. Olah and T.-L. Ho, *Synthesis*, **1976**, 610.

[3] D. H. R. Barton, J. C. Co J. F. McGarrity, and D. A. Widdowson, *J.C.S. Perkin I*, **1973**, 1565.