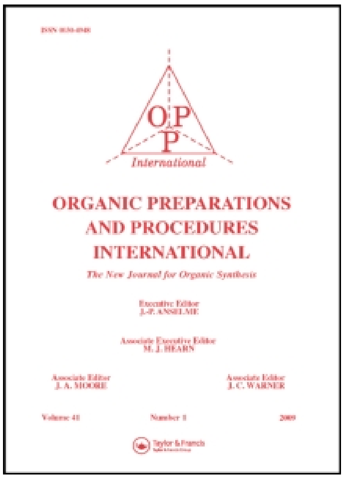


Organic Preparations and Procedures International
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

THE ELECTROCHEMICAL OXIDATIVE HYDROLYSIS OF KETONE OXIMES

M. R. van de Mark[a]; A. M. Scornavacca[a]
[a] Department of Chemistry, University of Miami, Coral Gables, Florida

To cite this Article van de Mark, M. R. and Scornavacca, A. M.(1981) 'THE ELECTROCHEMICAL OXIDATIVE HYDROLYSIS OF KETONE OXIMES', Organic Preparations and Procedures International, 13: 6, 395 — 399

To link to this Article: DOI: 10.1080/00304948109356150

URL: http://dx.doi.org/10.1080/00304948109356150

ORGANIC PREPARATIONS AND PROCEDURES INT. 13(6), 395-399 (1981)

THE ELECTROCHEMICAL OXIDATIVE HYDROLYSIS OF KETONE OXIMES

M. R. Van De Mark* and A. M. Scornavacca
Department of C hemistry, University of Miami
Coral Gables, Florida 33124

Recent findings on the ability of oxime dianions to direct alkylation with both regio- and stereochemical control has made oximes significant and potentially versatile synthetic intermediates.[1] Existing methodologies for regeneration of the carbonyl are somewhat limited.[2] We now report an anodic oxidative technique for the transformation ofoximes to the ketone in good yield.

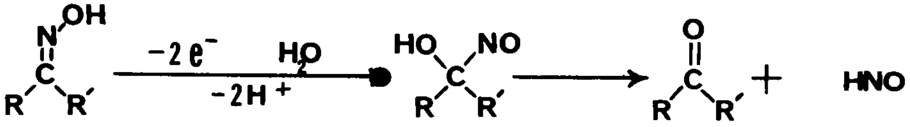
The transformation was accomplished by oxidation of the oxime at a graphite anode (and cathode) in a one compartment cell containing acetonitrile and water. Tetraethylammonium tetrafluoroborate was the supporting electrolyte. Table I illustrates the effect of solvent composition and current density on the yield of ketone. As the water content of the solvent increases the yield of the ketone increased. At low current densities (<500mA), the yield is also much higher. These observations are readily explained by the fact that the anodic process generates an acidic region which can either cause the Beckman (or abnormal) rearrangement or simply result in protonation of the oxime thus precluding its oxidation.

During electrolysis of the oximes, a faint blue color developed and remained throughout the work-up. However, upon distillation of the ketone, the color disappeared. The blue color is probably due to traces of a nitroso compound which may be an intermediate in the reaction (Scheme I). Iffland and Criner[3] as well as Kropf and Lambeck[4] have reported that the oxidation of oximes (such as cyclohexanone oxime) with lead tetraacetate produces the nitrosoacetate, a deep blue compound.

TABLE I. Cyclohexanone Oxime[a]

Solvent[b] Ratio	Current[c] i	Charge Passed F/Mole	% Yield of Ketone
99:1	0.5 A	2	0
95:5	0.5 A	2	10
90:10	0.5 A	2	25
80:20	0.5 A	2	59
80:20	1.0 A	2	21
80:20	0.3 A	2	63
80:20	0.2 A	4	68

a. 5g Cyclohexanone oxime in 150ml solvent containing 2g electrolyte at ten degrees. b. Acetonitrile to water ratio. c. Current shown is per 15 cm^2 electrode area.



SCHEME I

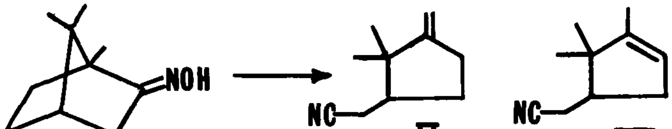
A brief survey of several aliphatic ketones demonstrates the versatility of the reaction (Table II). There is the possibility of acid-catalyzed Beckman rearrangement of the oximes. As is to be expected, the proton concentration near the surface of the electrode is a function of the current density, of the solvents ability to transport the proton to the cathode where it is reduced to hydrogen and of the stirring rate. Since the Beckman rearrangement usually requires a long contact time or elevated temperatures, the acidity near the electrode surface need not be eliminated only minimized. If the current density is maintained below $30mA/cm^2$ and the solvent is either buffered or the percentage of water maintained at 20%, the acidity will be minimized near the electrode. By careful choice of conditions the oximes can be maintained soluble in the media and rearrangement minimized or suppressed.

TABLE II.

Oxime^a	i^b	F/Mole	% Yield of Ketone
Cyclohexanone	0.2	4	68
2-Octanone	0.25	2	73
2-Octanone	0.2	4	90
4-t-Butylcyclohexanone	0.2	4	67
Camphor	0.15	4	3

a. Five grams of oxime in 150ml 20% aqueous acetonitrile containing 2 grams of electrolyte at 10°. b. Current shown is in amps/15cm^2 electrode area.

The electrochemical oxidation of camphor (I) represents a good example of the effect of acid generated by the anode. It is well known that camphor oxime is susceptible to acid-catalyzed abnormal Beckman.[5] The reaction leads predominatly to the two nitriles shown below. The anodic oxidation produced compounds II and III in equal amounts with a total



I II III

conversion of 38%. Also recovered starting material accounted for an additional 27%. The remaining material was unidentified due to the complexity. Compounds II and III under the electrolysis conditions are electroactive and would undergo oxidation analogously to those demonstrated by Shono with the oxidation of a variety of olefins.[6] Therefore the low yield of II and III may be due to further oxidation which would yield several new products. It should be noted that the conversion and ratio of products II and III are quite irreproducible unlike the yield of ketone.

The electrochemical oxidative removal of the oxime group appears to be a viable alternative to the current methodology. Its assets are the high yield, especially for linear or high molecular weight species, the low cost (very limited expenditures required since only a controlled current power supply is required) and finally the ease of work-up with no metal salts to remove.

EXPERIMENTAL

Power supply was either an EICO Model 1020 (0-36V, 0-0.2A) or Trygon Electronics Model RS60-7.5 (0-60V, 0-7.5A). A simple 12V battery charger is also sufficient. Graphite electrodes were 0.25" diameter Spectro Tech carbon rods available from Ultra Carbon Corporation (Cat. No. 731254/ ST-50). Electrolyte, tetraethylammonium tetrafluoroborate was obtained from Southwestern Analytical Chemicals. Acetonitrile was obtained from Burdic & Jackson and distilled from phopsphorous pentoxide. All ketones were AR grade and used without further purification. Oximes were prepared by standard procedures.[7]

Electrolysis were performed in a 250ml electrolytic beaker[8] with 150ml of solution containing 2 grams (0.01 mole) tetraethylammonium tetrafluoroborate as supporting electrolyte. Five grams of the oxime were added and stirred magnetically. Two graphite electrodes were mounted in a rubber stopper 1 1/2" apart and 3" into the solution (a vent hole was also required to avoid pressure build-up).

After passage of the requisite current, integrated with an Acromag Counter or a copper coulombmeter, the solution was concentrated by distillation to 50ml. Addition of 50ml water and extraction with four 50ml portions of ether, drying over sodium sulfate and concentration in vacuo yielded the crude ketones.

Analysis by gas chromatography produced the data shown in Tables I and II. Distillation followed by 2,4-dinitrophenylhydrazone derivatization yielded results consistent with the GC data. Matching infrared and proton nuclear magnetic resonance spectra were observed for all products with respect to authentic materials.

Acknowledgements.- We thank J.-P. Anselme for helpful discussions and the University of Miami for financial support for this work.

REFERENCES

1. a) M. E. Jung, P. A. Blair and J. A. Lowe, Tetrahedron Lett., 1439 (1976).
   b) R. E. Lyle, J. E. Saavedra, G. G. Lyle, H. M. Fribush and J. L. Marshall, ibid., 4431 (1976).
   c) R. E. Lyle, H. M. Fribush, G. G. Lyle, J. E. Saavedra, J. Org. Chem., 43, 1275 (1978).
2. I. T. Harrison and S. Harrison, "Compendium of Organic Synthetic Methods", Vol. I, Wiley-Interscience, New York, N.Y., 1971, p. 454.
3. a) D. C. Iffland and G. X. Criner, Chem. and Ind., 176 (1956).
   b) D. C. Iffland and G. X. Criner, M. Koral, F. J. Lotspelch, Z. B. Papanastassopi and S. M. White, J. Am. Chem. Soc., 75, 4044 (1953).
   c) D. C. Iffland and G. X. Criner, ibid., 75, 4047 (1953).
4. H. Kropf and R. Lambeck, Ann., 700, 18 (1966).
5. L. G. Donaruma and W. Z. Heldt, Org. Reactions, Vol. 11, John Wiley & Sons, New York, 1960, p. 1.
6. T. Shono and A. Ikeda, J. Am. Chem. Soc., 90, 178 (1972).
7. R. L. Shriner, R. C. Fuson and D. Y. Curtin, "The Systematic Identification of Organic Compounds", 5th Ed., John Wiley & Sons, New York, N.Y., 1964.
8. Electrolytic beakers, tall form beakers, are available from Kimble (14070).

(Received September 23, 1980; in revised form May 29, 1981)