UNCLASSIFIED

AD 296 573

Reproduced
by the

ARMED SERVICES TECHNICAL INFORMATION AGENCY
ARLINGTON HALL STATION
ARLINGTON 12, VIRGINIA

UNCLASSIFIED

NOTICE: When government or other drawings, specifications or other data are used for any purpose other than in connection with a definitely related government procurement operation, the U. S. Government thereby incurs no responsibility, nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use or sell any patented invention that may in any way be related thereto.

63-2-4

CATALOGED BY ASTIA
AS AD NO. 296573

296 573

Office of Naval Research

Contract No. N62558 - - - 2381
Task No. NR051 - - - 417

Technical Report No. 4

Reduction by Organometallic Complexes.

By David A. Brown, J. P. Hargaden and H. Sloan*

ASTIA
25 1963

*Present Address: Chemistry Department, University of Toronto,
Toronto, Canada.

In a recent paper (1), Wilkinson and co-workers discussed the protonation of transition metal carbonyl complexes; solutions of tricarbonylarenechromiums in concentrated acids were found to decompose rapidly but N.M.R. evidence for protonation at the metal atom was obtained under these conditions. Sternberg and Wender (2) have explained previously the reducing ability of the dicarbonyl-π-cyclopentadienyliron dimer in ethanolic hydrochloric acid in terms of protonation at the iron atom but no direct spectral evidence is available to support this contention (1). Publication of these results prompts us to record some preliminary observations of the behaviour of tricarbonylarene chromiums in dilute ethanolic hydrochloric acid which are consistent with the above view. We find that solutions of azobenzene (10^{-2} M) and tricarbonylarenechromiums (10^{-2}M), $RC_6H_5(CO)_3$, in dilute ethanolic hydrochloric acid (10^{-1}M) under nitrogen give fair yields (up to 30%) of benzidine dihydrochloride, identified by analysis and I.R. spectrum. The reaction occurs for the substituent range R=Me, CL, H, NH_2, NHMe and NMe_2 and is facilitated by electron repelling groups; this is consistent with protonation at the chromium aton being assisted by charge transfer as discussed by two of us previously (3). Moreover, no reduction is observed in the absence of acid so some type of protonation seems essential. More dilute solutions (10^{-4}M) of the complexes undergo fairly rapid decomposition (complete in 30 mins.-2 hours) in ethanolic hydrochloric acid under nitrogen with the evolution of carbon monoxide and formation of free arene. Spectrophotometric studies of tricarbonylanilinechromium show an immediate fall in intensity of the 3150 Å band corresponding to protonation at the nitrogen atom followed by a further decrease due to decomposition; extrapolation gives a pKa value of 1·26. In contrast, a rapid potentiometric titration, under nitrogen, gives a pKa of 2·15. The difference may be ascribed to additional protonation at the metal atom.

In the presence of an oxidant, reduction apparently occurs by proton transfer from the protonated complex with, consequently, less direct decomposition. Increase of reaction temperature favours the latter and the yields of benzidine are correspondingly lower. These results support the view that reduction by organometallic complexes is related to protonation at the metal atom. Detailed investigations of these reactions are in progress.

(1) Davison, McFarlane, Pratt and Wilkinson, J., 1962, 3653.

(2) Sternberg and Wender, Internat. Conf. Coordination Chemistry, Chem. Soc. Special Publ. No. 13, 1959, p. 35.

(3) Brown and Sloan, J., 1962, 3846.

TECHNICAL REPORT DISTRIBUTION LIST

Contract N62558-2381

NR No 051-417

Commanding Officer
Office of Naval Research Branch
Office
The John Crerar Library Building
86 East Randolph Street
Chicago 1, Illinois. (1)

Commanding Officer
Office of Naval Research Branch
Office
346 Broadway
New York 13, New York (1)

Commanding Officer
Office of Naval Research Branch
Office
1030 East Green Street
Pasadena 1, California (1)

Commanding Officer
Office of Naval Research Branch
Office
Box 39 Navy 100 Fleet Post Office
New York, New York (7)

Director, Naval Research Laboratory
Washington 25, D.C.
Attn: Technical Information Officer (6)
Chemistry Division (2)

Chief of Naval Research
Department of the Navy
Washington 25, D.C.
Attn: Code 425 (2)

DDR & E
Technical Library
Room 3C-128, The Pentagon
Washington 25, D.C. (1)

Technical Director
Research & Engineering Division
Office of the Quartermaster General
Department of the Army
Washington 25, D.C. (1)

Research Director
Clothing & Organic Materials Division
Quartermaster Research & Engineering
Command
U. S. Army
Natick, Mass. (1)

Air Force
Office of Scientific Research (SRC-E)
Washington 25, D.C. (1)

Commanding Officer
Diamond Ordnance Fuze Laboratories
Washington 25, D.C.
Attn: Technical Information Office
Branch 012 (1)

Office, Chief of Research & Development Department of the Army
Washington 25, D.C.
Attn: Physical Sciences Division (1)

Chief, Bureau of Ships
Department of the Navy
Washington 25, D.C.
Attn: Code 342C (2)

Chief, Bureau of Naval Weapons
Department of the Navy
Washington 25, D.C.
Attn: Technical Library (4)

ASTIA
Document Service Centre
Arlington Hall Station
Arlington 12, Virginia (10)

Director of Research
U.S. Army Signal Research &
Development Laboratory
Fort Monmouth, New Jersey (1)

Naval Radiological Defense Laboratory
San Francisco 24, California
Attn: Technical Library (1)

Naval Ordnance Test Station
China Lake, California
Attn: Head, Chemistry Division (1)

Commanding Officer
Army Research Office
Box CM, Duke Station
Durham, North Carolina
Attn: Scientific Synthesis Office (1)

Brookhaven National Laboratory
Chemistry Department
Upton, New York (1)

Atomic Energy Division
Division of Research
Chemistry Programmes
Washington 25, D.C. (1)

Atomic Energy Commission
Division of Technical Information Extension
Post Office Box 62
Oak Ridge, Tennessee (1)

U.S. Army Chemical Research and Development Laboratories
Technical Library
Army Chemical Centre, Maryland (1)

Office of Technical Services
Department of Commerce
Washington 25, D.C. (1)

Commanding Officer
Office of Naval Research Branch Office
1000 Geary Street
San Francisco 9, California
Attn: Dr. P. A. Miller (1)

Dr. G.Barth-Wehrenalp, Director
Inorganic Research Department
Pennsalt Chemicals Corporation
Box 4388
Philadelphia 18, Penn. (2)

Dr. A.B.Burg
Department of Chemistry
University of Southern California
Los Angeles 7, California (1)

Dr. T.G.Fox, Director of Research
Mellon Institute
Department of Chemistry
Pittsburgh 13, Penn. (1)

Dr. H.S.Gutowsky
Department of Chemistry
University of Illinois
Urbana, Illinois (1)

Dr. J.E.Leffler
Department of Chemistry
Florida State University
Tallahassee, Florida (1)

Dr. W.N.Lipscomb
Department of Chemistry
Harvard University
Cambridge, Mass. (1)

Dr. S. Y. Tyree, Jr.,
Department of Chemistry
University of North Carolina
Chapel Hill, North Carolina (1)

Mr. B.R.Stein
European Research Office
U.S. Army R. & D. Liaison
Group 985IDU
APO 757
New York, N.Y. (1)

Dr. M.J.S. Dewar
Department of Chemistry
University of Chicago
Chicago 37, Illinois (1)

Dr. M.S. Cohen, Chief
Propellants Synthesis Section
Reaction Motors Division
Denville, New Jersey (1)

POrdnance Corps (ORDBB-TO1)
Picatinny Arsenal
Dover, New Jersey (1)

Monsanto Research Corporation
Everett Station
Boston 49, Mass.
Attn: Mr. K. Warren Easley (1)

Dr. D.C.Bradley
Department of Chemistry
University of Western Ontario
London, Canada (1)

Dr. T.L.Heying
Organics Division
Olin Mathieson Chemical Corporation
275 Winchester Avenue
New Haven, Conn. (1)

Dr. Joyce J. Kaufman
RIAS
7212 Bellona Avenue
Baltimore 12, Maryland (1)

Dr. H.B.Jonasson
Department of Chemistry
Tulane University
New Orleans, Louisiana (1)

Dr. T.D.Parsons
Department of Chemistry
Oregon State College
Corvallis, Oregon (1)

Dr. J.D.Roberts
Department of Chemistry
California Institute of Technology
Pasadena, California (1)