it appears that all peptide bonds are routinely hydrolyzed. Amino acid analysis was performed with a Beckman amino acid analyzer which has an estimated accuracy of 5%.

Registry No.—DMF, 68-12-2; methylene chloride, 75-09-2.

Acknowledgment.—This work was supported by National Science Foundation Grant BG-7033X and National Institutes of Health Grant HD-01262 to Professor M. D. Kamen, and National Institutes of Health Grant GM-10928 to Professor J. Kraut. We are especially grateful to Professor M. D. Kamen whose continuing support and encouragement over several years has made our peptide synthesis laboratory possible.

Synthesis of α,α-Dinitro-N′-fluorodiimide N-Oxides[1]

KURT BAUM

Environmental Systems Division, Aerojet-General Corporation, Azusa, California 91702

Received February 17, 1970

Syntheses of N′-fluorodiimide N-oxides have been reported by reactions of tetrafluorohydrazine[2-6] or difluoramine[3,7] with nitroso compounds. Pseudonitroles gave α-nitro-N′-fluorodiimide N-oxides,[3,7] but α,α-dinitro-N′-fluorodiimide N-oxides have not been prepared directly; α,α-dinitro nitroso compounds are unknown.

$$R{-}NO + HNF_2 \longrightarrow R{-}\overset{\overset{O}{\uparrow}}{N}{=}NF + HF$$

$$R{-}NO + \cdot NF_2 \longrightarrow R{-}\overset{\overset{O}{\uparrow}}{N}{=}NF + [F\cdot]$$

In the present work, 1,1-dinitrobutyl-N′-fluorodiimide N-oxide was isolated from the reaction of the sodium salt of 1,1-dinitrobutane with tetrafluorohydrazine in methanol. The product was identified by analysis, and ir and nmr spectra. Most significantly, the ^{19}F signal, −125 ppm from trifluoroacetic acid, was in the region reported for other N′-fluorodiimide N-oxides. The mechanism for this reaction may involve 1,1-dinitro-1-nitrosobutane as a transient intermediate. The nitrosating agent may be nitrous acid resulting from the Neff reaction of the starting material; 1,1-dinitrobutane was also formed. An acid source is the abstraction of hydrogen from the solvent to give difluoramine which is readily dehydrofluorinated.

Preliminary work on this reaction was done with the salt of 1,1-dinitroethane, but the product was such a sensitive explosive that characterization could not be completed. The salt of nitroform did not react under these conditions. Sodium 2-propanenitronate on the other hand yielded only the coupling product, 2,3-dimethyl-2,3-dinitrobutane, as reported by Freeman.[8]

Experimental Section

Caution. Explosion shielding and remote manipulation are required for the N_2F_4 reaction and for product isolation.

1,1-Dinitrobutyl-N′-fluorodiimide N-Oxide.—A Fischer–Porter aerosol tube containing a solution of 14.8 g (0.10 mol) of 1,1-dinitrobutane and 0.10 mol of sodium methoxide in 45 ml of methanol was evacuated at liquid nitrogen temperature and filled with nitrogen several times. The tube was charged with 0.2 mol of tetrafluorohydrazine and the mixture was stirred for 20 hr at ambient temperature. The excess tetrafluorohydrazine was removed and most of the solvent was removed under vacuum. Methylene chloride (50 ml) was added and the solution was filtered and distilled to give 6.5 g of liquid, bp 46° (0.35 mm), which contained some 1,1-dinitrobutane. Chromatography with a 2 × 38 cm column of neutral active alumina and methylene chloride resulted in retention of the 1,1-dinitrobutane on the column as a bright yellow complex. Distillation of the eluent gave 1.3 g (6.2% yield) of 1,1-dinitro-1-butyl-N′-fluorodiimide N-oxide, bp 34–35° (0.15 mm).

Anal. Calcd for $C_4H_7N_4FO_5$: C, 22.86; H, 3.33; N, 26.7; F, 9.05. Found: C, 23.20; H, 3.17; N, 26.63; F, 9.0.

The proton nmr spectrum consisted of a triplet (J = 8 Hz) at δ 1.12 for CH_3, a multiplet at δ 1.9 for CH_3CH_2, and a triplet (J = 8 Hz) at δ 3.12 for the other methylene. The fluorine spectrum consisted of a broadened singlet at −125 ppm from external trifluoroacetic acid. The infrared spectrum consisted of bands at 3.42 (m), 3.53 (m), 6.4 (vs), 6.9 (m), 7.01 (m), 7.3 (m), 7.54 (s), 9.05 (w), 10.8 (w), 11.7 (m), 12.4 (m), and 13.2 μ (m).

Registry No.—1,1-Dinitrobutyl-N′-fluoridiimide N-oxide, 24903-89-7.

(1) This work was supported by the Office of Naval Research.

(2) J. W. Frazer, B. E. Holder, and E. F. Worden, *J. Inorg. Nucl. Chem.*, **24**, 45 (1962).

(3) T. E. Stevens and J. P. Freeman, *J. Org. Chem.*, **29**, 2279 (1964).

(4) I. L. Knunyants, B. L. Dyatkin, and R. A. Becker, *Dokl. Akad. Nauk SSSR*, **170**, 337 (1966).

(5) A. N. Medvedev, K. N. Smirnov, S. S. Dubov, and V. A. Ginsburg, *Zh. Obshch. Khim.*, **38**, 2462 (1968).

(6) S. F. Reed, Jr., *J. Org. Chem.*, **32**, 3869 (1967).

(7) K. Baum, *ibid.*, **34**, 2049 (1969).

(8) J. P. Freeman, *Inorg. Chim. Acta Rev.*, **1**, 65 (1967).

Radical Anions Produced by Electrochemical Reduction of 1,3 Diketones[1]

R. C. BUCHTA AND D. H. EVANS

Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706

Received February 17, 1970

The half-life of radicals obtained by electrolysis of enolized 1,3 diketones is short because of rapid coupling reactions.[2] In DMSO as solvent, the reduction of the enolate anion of a 1,3 diketone causes decomposition *via* cleavage reactions.[2b] This latter fact appears to be inconsistent with one aspect of the pioneering work of Bauld and coworkers on the electron spin resonance (esr) spectra of dianion radicals.[3-6] These workers reported[6] esr data for the dianion radical formed by the electrochemical reduction of the dibenzoylmethide ion in DMF. On the basis of our observations of the electrochemical behavior of 1,3 diketones, we suggest that

(1) This work was supported by Grant No. GP-8350, National Science Foundation. Support for computing was provided by the National Science Foundation and the Wisconsin Alumni Research Foundation.

(2) (a) R. C. Buchta and D. H. Evans, *Anal. Chem.*, **40**, 2181 (1968); (b) R. C. Buchta, Ph.D. Thesis, University of Wisconsin, 1969.

(3) N. L. Bauld, *J. Amer. Chem. Soc.*, **86**, 2305 (1964).

(4) N. L. Bauld and M. S. Brown, *ibid.*, **87**, 4390 (1965).

(5) N. L. Bauld and J. Zoeller, *Tetrahedron Lett.*, 885 (1967).

(6) N. L. Bauld and M. S. Brown, *J. Amer. Chem. Soc.*, **89**, 5413, 5417 (1967).

the spectrum obtained by Bauld and Brown[6] is actually that of the radical anion of 1-phenyl-1,2-propanedione rather than the dianion radical of dibenzoylmethane.

In Figure 1 the experimental spectrum (B) obtained from electrochemical reduction of dibenzoylmethide in DMF and the simulated spectrum (A) based on anticipated splitting constants for dibenzoylmethane dianion radical are reproduced from the original paper.[6] Also included is a simulated spectrum for the anion radical of 1-phenyl-1,2-propanedione using published splitting constants.[1,7,8] In spite of the relatively large line widths (*ca.* 0.2 gauss) the excellent agreement between the experimental spectrum (B) and the spectrum simulated for the 1-phenyl-1,2-propanedione radical anion (C) suggests that an unexpected reaction sequence is leading to the formation of the 1,2-diketone during electrochemical reduction of dibenzoylmethide.

In DMSO as solvent, several experiments demonstrate that the reduction of dibenzoylmethide is not a simple one electron process yielding the dianion radical. (1) Controlled potential coulometry at a potential cathodic of the half-wave potential of dibenzoylmethide ($E_{1/2}$ = −2.25 V *vs.* sce, 0.1 *M* tetra-*n*-butylammonium perchlorate in DMSO) resulted in a prolonged electrolysis with a total uptake of 3–4 electrons per dibenzoylmethide ion. (2) Cyclic voltammetric experiments indicated that the product of the reduction of dibenzoylmethide decomposed with a half-life of the order of 0.1 second. (3) Room temperature electrochemical reduction of dibenozylmethide in a cell in the esr spectrometer microwave cavity produced acetophenone radical anion. The observed splitting constants were identical with those reported for acetophenone radical anion in 1,2-dimethoxyethane.[9]

The mechanism by which acetophenone is produced is not known though either cleavage of the dianion radical itself or cleavage of the dibenzoylmethide catalyzed by bases generated during electrolysis seems likely. In any case, the production of acetophenone during the electrolysis provides a clue to the source of the 1-phenyl-1,2-propanedione radical anion detected by Bauld and Brown.[6]

In the original study[7] of the electrolytic reduction of acetophenone in DMF, an esr spectrum was obtained which proved to be inconsistent with the expected splitting constants for acetophenone radical anion. The species causing this spectrum was later identified[8] as the radical anion of 1-phenyl-1,2-propanedione. This unexpected product has only been observed when DMF is used as solvent. In DMSO or dimethoxyethane only the acetophenone radical anion is formed. It has been suggested[8] that in DMF the dianion of acetophenone may abstract a carbonyl group from the solvent. This is consistent with the observation[9] that the radical anion of 1-phenyl-1,2-propanedione is obtained only at potentials on the second polarographic wave of acetophenone in DMF.

We find that acetophenone radical anion is produced during reduction of dibenzoylmethide in DMF just as it is in DMSO. We suggest that under the conditions employed by Bauld and Brown[6] for the electrolysis of dibenzoylmethide in DMF, the acetophenone produced

(7) P. H. Rieger and G. K. Fraenkel, *J. Chem. Phys.*, **37**, 2811 (1962).
(8) G. A. Russell, E. T. Strom, E. R. Talaty, and S. A. Weiner, *J. Amer. Chem. Soc.*, **88**, 1998 (1966).
(9) N. Steinberger and G. K. Fraenkel, *J. Chem. Phys.*, **40**, 723 (1964).

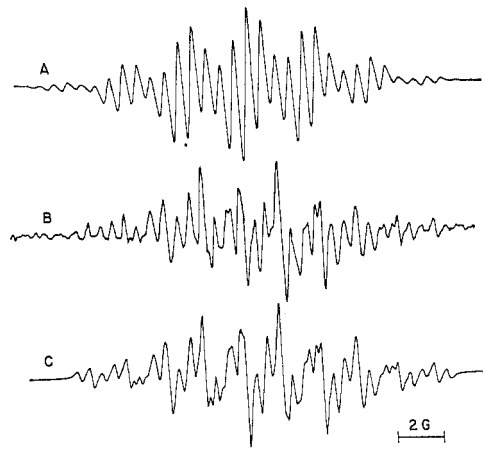

Figure 1.—A. Computer simulated esr spectrum for the dianion radical of dibenzoylmethide.[6] B. Experimental esr spectrum obtained by electrochemical reduction of dibenzoylmethide in DMF.[6] C. Computer simulated spectrum for the radical anion of 1-phenyl-1,2-propanedione.

by cleavage of dibenzoylmethide reacted further to produce 1-phenyl-1,2-propanedione radical anion which gave the spectrum in Figure 1B. This reassignment pertains only to the spectrum reported from electrochemical reduction of dibenzoylmethide in DMF. The partially resolved spectra obtained by chemical reduction in other solvents are probably due to the dianion radical as originally stated.[6]

Cleavage reactions are frequently encountered during the electrochemical reduction of 1,3-diketones. For example 2-*t*-butyl-1,3-diphenyl-1,3-propanedione is reduced ($E_{1/2}$ = −1.80 V *vs.* sce; controlled potential coulometric *n*-value = 1.1 equivalents/mol) to the radical anion of 3,3-dimethyl-1-phenyl-1-butanone (five nonequivalent ring protons with splitting constants of 6.40, 4.25, 3.54, 1.10 and 0.82 gauss; two equivalent methylene protons with splitting constant of 4.21 gauss). Other products of the cleavage reaction were not identified.

A 1,3-diketone giving a relatively stable radical anion is 2,2-dimethyl-1,3-diphenyl-1,3-propanedione. Its radical anion may be produced by controlled potential reduction ($E_{1/2}$ = −1.78 V *vs.* sce; *n*-value = 0.99 equivalents/mol). The spectrum was in agreement with the following assignment of splitting constants: six equivalent protons (*ortho* and *para*), 2.30 gauss; ten equivalent protons (*meta* and methyl), 0.50 gauss.

The radical slowly decomposes in DMSO yielding isobutyrophenone which may be identified in the electrolysis solution by polarography ($E_{1/2}$ = −2.03 V *vs.* sce) and by its esr spectrum obtained by further electrolysis of the above solution. The spectrum was identical with that obtained using authentic isobutyrophenone (splitting constant for α-proton: *ca.* 2.5 gauss. Very broad lines (0.4 gauss) are probably caused by unresolved methyl proton splittings).

The protons consumed in the formation of acetophenone during the electrolysis of dibenzoylmethide originate in the solvent. This was demonstrated by the acquisition of the esr spectrum of the radical anion of d_3-acetophenone during reduction of undeuterated dibenzoylmethide in d_6-DMSO. The splitting constant for the three methyl deuterons was 1.04 gauss and the ring proton splittings were unaffected by the deu-

terium substitution. No deuterium–hydrogen exchange was detectable by nmr in a solution of dibenzoylmethide and tetra-*n*-butylammonium perchlorate in d_6-DMSO indicating that no deuteration occurs prior to electrolysis.

Spectra may be obtained by electrolysis of dibenzoylmethane in THF at −60° or by electrolysis of dibenzoylmethane in DMSO containing 0.1 *M* tetra-*n*-butylammonium dibenzoylmethide at room temperature. These spectra are different than any so far reported for this system (benzil,[1] acetophenone, 1-phenyl-1,2-propanedione[6]) but unambiguous analyses of the spectra have not been attained. Definite assignment must await further studies now in progress.

Experimental Section

A Sargent Model XV polarograph with a Sargent IR compensator was used with a three electrode polarographic cell.[2a] The reference electrode was an aqueous saturated calomel electrode. The potentiostat for controlled potential coulometry was a Wenking Model 61 RS. The working electrode in the controlled potential electrolysis cell[2a] was a 30 cm² mercury pool. Cyclic voltammetric instrumentation was of conventional[10] design. The working electrode for cyclic voltammetry was a hanging mercury drop electrode (Model E410, Brinkmann Instruments) used in the polarographic cell mentioned above. The esr spectrometer was a Varian E-3. A Varian electrolytic cell was used for generation of radicals in the microwave cavity. The computer program for simulation of esr spectra was similar to that employed by Stone and Maki.[11]

Reagent grade DMSO was stirred over calcium hydride for at least 12 hr and distilled at reduced pressure just before use. Tetra-*n*-butylammonium perchlorate (Matheson) was used as received except for the cyclic voltammetric studies where it was recrystallized from ethyl acetate and vacuum dried. The dibenzoylmethide ion was prepared as its tetra-*n*-butylammonium salt.[2a] The 2-*t*-butyl-1,3-diphenyl-1,3-propanedione was prepared by a procedure analogous to the reported synthesis of 3-*t*-butyl-2,4-pentanedione:[12] mp 124.5–125°; nmr (CCl_4) δ 1.15 (s, 9, CH_3), 5.22 (s, 1, methine), 7.38 (m, 6, aromatic), 7.92 (m, 4, aromatic). *Anal.* Calcd for $C_{19}H_{20}O_2$: C, 81.40; H, 7.19. Found: C, 81.59; H, 7.23. The 2,2-dimethyl-1,3-diphenyl-1,3-propanedione was prepared as described previously:[13] mp 97.5–98° (99°);[13] nmr ($CDCl_3$) δ 1.67 (s, 6, CH_3), 7.33 (m, 6, aromatic), 7.85 (m, 4, aromatic).

(10) W. L. Underkofler and I. Shain, *Anal. Chem.*, **35**, 1778 (1963).
(11) E. W. Stone and A. H. Maki, *J. Chem. Phys.*, **38**, 1999 (1963).
(12) P. Boldt and H. Militzer, *Tetrahedron Lett.*, 3599 (1966).
(13) I. Smedley, *J. Chem. Soc.*, **97**, 1484 (1910).

Production of Linear Acids or Esters by the Platinum–Tin-Catalyzed Carbonylation of α Olefins

L. J. KEHOE AND R. A. SCHELL

Research Laboratories, Ethyl Corporation, Ferndale, Michigan 48220

Received February 19, 1970

The carbonylation reaction of olefins in the presence of metal carbonyls or carbonyl precursors to form acids or esters was developed by Reppe and his coworkers.[1] For example, the reaction of ethylene with CO and water in the presence of nickel salts or nickel carbonyl yields propionic acid. When olefins larger than ethylene are reacted, the products consist of large amounts of branched isomers, in addition to the desired linear product, *i.e.*

$$RCH{=}CH_2 + CO + CH_3OH \longrightarrow RCH_2CH_2\overset{\overset{O}{\|}}{C}OCH_3 + RCH(CH_3)\overset{\overset{O}{\|}}{C}OCH_3$$

Furthermore, these reactions are generally carried out at temperatures above 150°, and a variety of other side reactions including polymerization, isomerization, and reduction can compete with the carbonylation.

Recent reports describe successful olefin carbonylation under relatively mild conditions which can avoid many of these competing reactions. Both palladium[2,3] and platinum[4] complexes were found to be catalytically active below 100°. However, none of these systems, as described, offers the combination of excellent yields and a high degree of product linearity. While systems for the formation of highly linear aldehydes[5,6] or alcohols[7] from α olefins are known, the purpose of this note is to describe a catalyst system that will effect rapid conversion of α olefins to highly linear acids or esters.

Jenner and Lindsey[4] found that a platinum salt–tin salt couple catalyzed the formation of esters from olefins at relatively low temperatures. However, their work was limited to olefins with less than six carbon atoms, and very high pressures (~800–1000 atm) with long reaction times (usually 10–16 hr) were necessitated. Additionally, propylene, the only straight chain, α monoolefin reported, gave a product mixture containing approximately equal amounts of methyl *n*-butyrate and methyl isobutyrate.

By utilizing a solvent such as acetone, methyl isobutyl ketone or 1,2-dimethoxyethane, and carefully controlling the reaction conditions, it has now been found that a H_2PtCl_6–$SnCl_2$ couple will catalyze carbonylation of olefins such as dodecene-1, in the presence of methanol, to highly linear (~85%) esters in 1 hr at 200 atm. The system has also been extended to acid synthesis under essentially the same conditions, by substituting water for the methanol. A typical reaction was carried out at 90° and 3000 psig of CO, with 1 mol % of H_2PtCl_6 and 5 mol % of $SnCl_2$ as catalyst, and acetone as solvent. Dodecene-1 conversion was 100% and product yield approximately 80% regardless of whether H_2O or methanol was utilized in the reaction. A small amount of olefin reduction occurred (2–4% of the olefin), but isomerization of the α olefin to internal olefins (mostly the 2-isomer) was the only major competing reaction. The acid (or ester) product was composed of approximately 85% of the straight chain isomer and 15% branched isomers. A mass spectral study showed that 80% of the branched product was the 2-methyl isomer.

(1) For extensive reviews of this work see: (a) C. W. Bird, *Chem. Rev.*, **62**, 283 (1962); (b) Ya. T. Eidus and K. Puzitakii, *Russ. Chem. Rev.*, **33**, 438 (1964).
(2) K. Bittler, N. V. Kutepow, D. Neubauer, and H. Reis, *Angew. Chem., Int. Ed. Engl.*, **7**, 329 (1968).
(3) J. Tsuji, *Accounts Chem. Res.*, **2**, 144 (1969).
(4) E. Jenner and R. V. Lindsey, Jr., U.S. Patent 2,876,254 (1959), DuPont.
(5) R. Pruett and J. Smith, *J. Org. Chem.*, **34**, 327 (1969).
(6) D. Evans, J. A. Osborn, and G. Wilkinson, *J. Chem. Soc. A*, 3133 (1968).
(7) L. Slaugh and R. Mullineaux, *J. Organometal. Chem.*, **13**, 469 (1968).