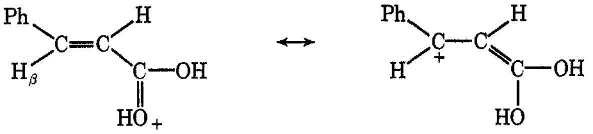
hydrogen, suggesting a significant amount of positive charge on the β carbon. Further studies into the hindered rotation about the C–O partial double bond are being pursued in this laboratory.



Thus there is no evidence for protonation of the –C=C– of maleic and fumaric acids in strong acids. The relationship of this observation to the path of enzymatic catalyzed cis–trans isomerization is not clear. It does seem that, if the enzyme-catalyzed reaction is indeed proceeding *via* carbon protonation, then there must be in the enzyme a highly specific arrangement of the active site, forcing the proton onto carbon rather than onto the more basic carboxyl group.

Experimental Section

Materials.—All compounds were commercially available and were distilled or recrystallized before use. All compounds were dried thoroughly, liquids over 4 Å molecular sieves and solids over P_2O_5 under vacuum.

Spectra.—Room-temperature nmr spectra were recorded on a Varian A-60 spectrometer. All chemical shifts (δ) are reported in parts per million relative to internal tetramethylamonium bromide taken as δ 3.2.

Low-temperature spectra were recorded on a Varian HA-100 spectrometer equipped with a variable-temperature probe.

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Notes

Reaction of Nitroxyl Radicals with Metal Carbonyls

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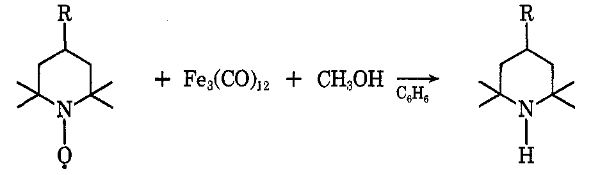
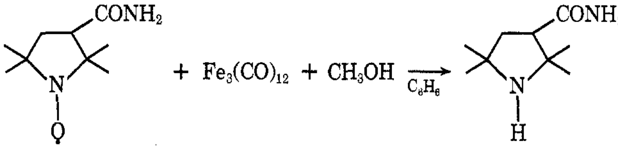
Deoxygenation reactions have been observed from treatment of sulfoxides,[1] amine oxides,[2] azoxy compounds,[2,3] nitrones,[2] and *C*-nitroso compounds[2,3] with iron pentacarbonyl [$Fe(CO)_5$]; nitro compounds with $Fe(CO)_5$,[2,4] diiron enneacarbonyl [$Fe_2(CO)_9$],[4] or triiron dodecacarbonyl [$Fe_3(CO)_{12}$–methanolic benzene];[5] *N*-nitroso compounds with $Fe(CO)_5$[2] or group VI metal carbonyls;[6] and *N*-phenyl-2-oxa-3-azabicyclo-[2.2.2]octene-5 with $Fe_2(CO)_9$.[7] There have been no reports, to the author's knowledge, of the reaction of metal carbonyls with nitroxyl radicals, an important group of compounds[8,9] potentially capable of undergoing deoxygenation to amino radicals. This note describes the reaction of iron carbonyls and group VI metal carbonyls with nitroxyl radicals.



1, R = H
3, R = $NHCOCH_3$

2, R = H
4, R = $NHCOCH_3$

Reaction of 2,2,6,6-tetramethylpiperidine-1-oxyl (**1**) with either $Fe(CO)_5$ in hot benzene or $Fe_2(CO)_9$ in benzene at room temperature gave a very unstable non-carbonyl containing organometallic compound. No amine was isolated from these reactions. However, treatment of **1** with $Fe_3(CO)_{12}$ in benzene containing a small amount of methanol (conditions under which the hydridoundecacarbonyltriferrate anion is generated)[5] did result in the formation of the deoxygenated product **2** in 42% yield. Similarly, 4-acetamido-2,2,6,6-tetramethylpiperidine-1-oxyl (**3**) gave the amine **4** in 55% yield and **6** was obtained from **5** in 41% yield. Therefore, $Fe_3(CO)_{12}$ is a useful reagent for reducing nitroxyl radicals to amines.[10] No bipiperidyl or bipyrrolidyl derivatives were produced in these reactions,[11] although small amounts of *N*-formyl amines[4,6,12] were apparently formed.



5 **6**

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[1] H. Alper and E. C. H. Keung, *Tetrahedron Lett.*, 53 (1970).

[2] H. Alper and J. T. Edward, *Can. J. Chem.*, **48**, 1543 (1970).

[3] A. S. Filatov and M. A. Englin, *Zh. Obshch. Khim.*, **39**, 783 (1969); *J. Gen. Chem. USSR*, **39**, 743 (1969).

[4] H. Alper, *Inorg. Chem.*, **11**, 976 (1972).

[5] J. M. Landsberg, L. Katz, and C. Olsen, *J. Org. Chem.*, **37**, 930 (1972).

[6] H. Alper, *Organometal. Chem. Syn.*, **1**, 69 (1970).

[7] Y. Becker, A. Eisenstadt, and Y. Shvo, *Tetrahedron Lett.*, 3183 (1972).

[8] E. G. Rozantsev, "Free Nitroxyl Radicals," Plenum Press, New York, N. Y., 1970.

[9] O. H. Griffith and A. S. Waggoner, *Accounts Chem. Res.*, **2**, 17 (1969).

[10] For other reductive methods, see N. Kornblum and H. W. Pinnick, *J. Org. Chem.*, **37**, 2050 (1972), and references cited therein.

[11] D. Mackay and W. A. Waters, *J. Chem. Soc. C*, 813 (1966), unsuccessfully attempted to prepare bi(2,2,6,6-tetramethyl)piperidyl from *N*-nitroso-2,2,6,6-tetramethylpiperidine.

[12] W. F. Edgell, M. T. Yang, B. J. Bulkin, R. Bayer, and N. Koizumi, *J. Amer. Chem. Soc.*, **87**, 3080 (1965).

Treatment of **1** with molybdenum hexacarbonyl in refluxing *n*-hexane gave an off-white diamagnetic substance whose elemental analysis and vapor pressure osmometric molecular weight determination indicated the composition $(C_9H_{18}NO)_2Mo_3$. The infrared (ir) spectrum of the product (KBr) showed *no* terminal metal carbonyl stretching bands (2100–1800 cm^{-1}) but did exhibit intense absorption at 960, 926, and 808 cm^{-1} due, at least in part, to N–O stretching with oxygen coordination to the metal. The mass spectrum was similar to that reported by Morrison and Davies[13] for **1**. Although the structure of the product is not known, it is clear that deoxygenation does not occur here, in contrast to the results with $Fe_3(CO)_{12}$. Tungsten hexacarbonyl reacted with **1** to give a solid analogous to that obtained using $Mo(CO)_6$. Chromium hexacarbonyl failed to react with **1** under the described conditions.

Experimental Section

Melting points were determined on a Fisher-Johns or Gallenkamp apparatus and are uncorrected. Boiling points are also uncorrected. Elemental analyses were carried out by A. Bernhardt, West Germany, and Meade Microanalytical Laboratory, Amherst, Mass. Infrared spectra were obtained on a Perkin-Elmer 457 spectrophotometer; the wavelength readings were calibrated with polystyrene film. Nmr spectra were obtained on a Varian A-60 spectrometer, employing tetramethylsilane as the internal standard.

The three iron carbonyls and chromium hexacarbonyl were purchased from Pressure Chemical Co. and were used as received. Climax Molybdenum Co. provided $Mo(CO)_6$ and $W(CO)_6$. Mr. William Moore prepared **1** following Rozantsev's procedure.[14] Radicals **3** and **5** were commercial products. All reactions were run under a nitrogen atmosphere.

Deoxygenation of Nitroxyl Radicals by $Fe_3(CO)_{12}$.—A mixture of $Fe_3(CO)_{12}$ (4.50 g, ~9 mmol), absolute methanol (2.0 ml), and dry benzene (50 ml) was refluxed with stirring for 6 hr. The nitroxyl radical (10 mmol), solid or in benzene (10–17 ml), was added to the iron hydride solution and the mixture was then refluxed for 9–18 hr. The solution was cooled and filtered, and work-up was effected in the following manner for the various reactions.

A. 2,2,6,6-Tetramethylpiperidine-1-oxyl.—The ir spectrum (neat) of the red oil, obtained on flash evaporation of the filtrate, showed it to consist largely of **2**, but a weak carbonyl stretching absorption at 1665 cm^{-1} indicated the possible presence of a small amount of *N*-formyl-2,2,6,6-tetramethylpiperidine. This by-product was also formed in reactions of **3** and **5**, but in all instances analytically pure samples could not be obtained owing to contamination by a metal carbonyl complex. The oil was repeatedly triturated with pentane. Flash evaporation of the dried pentane extract and subsequent distillation of the residue gave 0.59 g (42%) of 2,2,6,6-tetramethylpiperidine, bp 153–155° (lit.[15] bp 151–152°), identified by comparison with an authentic sample.

B. 4-Acetamido-2,2,6,6-tetramethylpiperidine-1-oxyl.—The filtered material was washed well with dry ether, and the washings were added to the filtrate. Flash evaporation of the filtrate gave an oil, which was dissolved in ether. Pentane was then added until precipitation of **4** was complete. Filtration gave 1.10 g (55%) of 4-acetamido-2,2,6,6-tetramethylpiperidine, mp 118–120° (lit.[16] mp 120°).

C. 3-Carbamoyl-2,2,5,5-tetramethylpyrrolidine-1-oxyl.—The filtered material was washed well with chloroform. Work-up as described in B gave **6** in 41% yield, mp 126.5–128.0° (lit.[17] mp 129–130°).

Reaction of 2,2,6,6-Tetramethylpiperidine-1-oxyl (1) with Group VI Metal Carbonyls.—A mixture of **1** (0.60 g, 3.85 mmol), $Mo(CO)_6$ (1.21 g, 4.63 mmol), and dry hexane (35 ml) was refluxed for 1 day. The solution was filtered hot, the filtrate depositing more solid on cooling. After refiltration, the solid was vacuum sublimed at 50° to remove any unreacted $Mo(CO)_6$. The off-white solid decomposed without melting at >210°: ir (KBr) 960 (s), 926 (s), 808 (s-vs), 613 (s), and 573 cm^{-1} (m); nmr (DMSO-d_6) δ 1.08 (s), 1.36 (s), 1.48 (s), 1.56 (m).

Anal. Calcd for $C_{18}H_{36}Mo_3N_2O_2$: C, 36.04; H, 6.04; N, 4.66; Mo, 47.91; mol wt, 600. Found: C, 36.79; H, 6.00; N, 4.25; Mo, 47.50; mol wt, 618 (osmometry, $CHCl_3$).

Tungsten hexacarbonyl reacted with **1** to give a white solid having no melting point below 300°, ir (KBr) 979 (s), 958 (s, sh), 890 (w-m), 814 (vs), 448 cm^{-1} (m).

Anal. Calcd for $C_{18}H_{36}N_2O_2W_3$: C, 25.09; H, 4.20; N, 3.24; W, 63.83. Found: C, 25.76; H, 4.85; N, 3.21; W, 62.99.

2,2,6,6-Tetramethylpiperidine-1-oxyl was inert to $Cr(CO)_6$ under the reaction conditions used for $Mo(CO)_6$.

Registry No.—**1**, 2564-83-2; $Mo(CO)_6$, 13939-06-5; $C_{18}H_{36}Mo_3N_2O_2$, 37213-92-6; $W(CO)_6$, 14040-11-0; $C_{18}H_{36}N_2O_2W_3$, 37213-93-7.

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[13] A. Morrison and A. P. Davies, *Org. Mass Spectrom.*, **3**, 353 (1970).

[14] Reference 8, p 217.

[15] N. Leonard and E. Nommensen, *J. Amer. Chem. Soc.*, **71**, 2808 (1949).

[16] E. G. Rozantsev and Y. V. Kokhanov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1477 (1966); *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, **15**, 1422 (1966).

[17] H. Pauly, *Justus Liebigs Ann. Chem.*, **322**, 113 (1902).

A Mild, Nonacidic Method for Converting Secondary Nitro Compounds into Ketones

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The utility in synthesis of the mainfold transformations of nitroparaffins and nitro olefins[1] would be considerably enhanced if facile methods for converting nitro groups into carbonyl groups were at hand, and, indeed, there has recently been renewed interest in such transformations, especially as they relate to the synthesis of 1,4 diketones.[2,3] The purpose of this note is to describe a simple and effective method for converting secondary nitro compounds into ketones and diketones which does not use acids[4] or oxidizing[5] or reducing agents.[2] Its usefulness may be gauged from the data presented in Table I, especially if it is borne in mind that the yields of ketones and 1,4 diketones refer to pure, isolated products.

Our procedure derives from an observation reported in 1956 which appears to have been little, if at all, noticed, namely that 2-nitrooctane, while unaffected by

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[1] (a) Houben-Weyl, "Methoden der Organischen Chemie," 4th ed, E. Müller, Ed., Vol. X, part 1, Georg Thieme Verlag, Stuttgart, 1971. (b) "The Chemistry of the Nitro and Nitroso Groups," H. Feuer, Ed., part 2, Interscience-Wiley, New York, N. Y., 1970, Chapter 3. (c) E. D. Bergmann, D. Ginsberg, and R. Pappo, *Org. React.*, **10**, 179 (1959).

[2] J. E. McMurry and J. Melton, *J. Amer. Chem. Soc.*, **93**, 5309 (1971).

[3] D. St. C. Black, *Tetrahedron Lett.*, 1331 (1972).

[4] The Nef reaction [W. E. Noland, *Chem. Rev.*, **55**, 137 (1955)] involves the action of base to form the nitroparaffin salt which is then treated with a mineral acid. In the most recent paper[3] on the subject, 3 *N* hydrochloric acid is employed. The reductive procedure of McMurry and Melton[2] also involves acidic solutions.

[5] H. Shechter and F. T. Williams [*J. Org. Chem.*, **27**, 3699 (1962)] have described the permanganate oxidation of nitroparaffin salts to aldehydes and ketones.