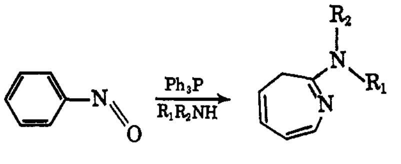
For example, reduction of *o*-nitrobutylbenzene with triethyl phosphite[1] yields a distribution of products strikingly similar to that obtained on pyrolysis of *o*-azidobutylbenzene,[2] and ring closure on treatment of *o*-nitrosobiphenyl[3] or *o*-nitrobiphenyl[4] with triethyl phosphite or triphenylphosphine is analogous to the thermolytic conversion of *o*-azidobiphenyl into carbazole.[5] These deoxygenation reactions among others[6] are considered by many authors[1,3,4,6] to proceed possibly *via* nitrene intermediates.

We wish to report that deoxygenation of nitrosobenzene with either triphenylphosphine or tributylphosphine in amine solvents results in ring enlargement with the ultimate formation of N-alkyl derivatives of 2-amino-3H-azepines. Similar products have been reported earlier for the photolysis[7] and pyrolysis[8] of phenyl azide in amines.



In a typical experiment, an ethereal solution of nitrosobenzene was added to a refluxing solution of triphenylphosphine in diethylamine. The work-up consisted of distillation of excess solvent and separation of the partially crystalline residue into solid and liquid fractions which were handled separately. The solid, after recrystallization from ethanol, afforded a 70% yield of triphenylphosphine oxide, mp 155.5–156.6°. On distillation the liquid yielded 2-diethylamino-3H-azepine[9] (62%), bp 59.0–61.0° (0.1 mm), $n^{25.5}$ 1.5513.

The yields of alkyl-2-amino-3H-azepine and triphenylphosphine oxide are markedly dependent on the amine. Both decrease with decreasing molecular weight of amine (see Table I). The reaction takes a different course in liquid ammonia, yielding only 18% of triphenylphosphine oxide and trace amounts of aniline[10] as the only basic product. Triphenylphosphine appears to be moderately more effective than tributylphosphine on the basis of comparable experiments in dimethylamine (Table I).

Elemental analysis of the three new alkyl-2-amino-3H-azepines are satisfactory. The infrared spectra of all these azepines are characterized by two strong absorption bands between 1500 and 1600 cm^{-1}: R_1 (C_2H_5), R_2 (C_2H_5) at 1510 and 1560 cm^{-1}; R_1 (n-C_4H_9), R_2 (H) at 1522 and 1599 cm^{-1}; R_1 (CH_3), R_2 (CH_3) at 1510–1560 cm^{-1}; R_1 (CH_3), R_2 (H) at 1522 and 1590 cm^{-1}.

Table I. Yields of Alkyl-3H-azepine and Triphenylphosphine Oxide for Various Amines

Amine		Yield, %	
R_1	R_2	Azepine	Phosphine oxide
C_2H_5	C_2H_5	62	70
n-C_4H_9	H	60	70
CH_3	CH_3	50	65
CH_3	H	4	34

A detailed analysis of the nmr spectrum of 2-diethylamino-3H-azepine and the concomitant basis for structural assignment have been described recently.[7] The portions of the other spectra assigned to the seven ring protons are remarkably similar and, therefore, subject to a similar analysis. A generalized description of all four spectra follows:[11] a quartet (2 H) which appears to be the superpositions of two triplets, in the range τ 7.49–7.39; a quartet in the range τ 4.87–5.00; a quartet in the range τ 4.28–4.38; a quartet in the range τ 3.73–3.80; a doublet in the range τ 2.95–3.04.

Phenyl nitrene and 7-azabicyclo[4.1.0]hepta-2,4,6-triene have been hypothesized as intermediates in the rearrangement of phenyl azide.[7,8] On the basis of this work and that of Sundberg,[1] the same hypothesis is reasonable for the rearrangement of nitrosobenzene.

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(1) R. J. Sundberg, *Tetrahedron Letters*, 477 (1966).

(2) G. Smolinsky and B. I. Feuer, *J. Org. Chem.*, **29**, 3097 (1964).

(3) P. J. Bunyon and J. I. G. Cadogan, *J. Chem. Soc.*, 42 (1963).

(4) J. I. G. Cadogan, M. Cameron-Wood, R. K. Mackie, and R. J. G. Searle, *J. Chem. Soc.*, 4831 (1965).

(5) P. A. S. Smith and B. B. Brown, *J. Am. Chem. Soc.*, **73**, 2435 (1951).

(6) For references to other deoxygenation reactions, see the excellent review on imidogens (nitrenes) by R. A. Abramovitch and B. A. Davis, *Chem. Rev.*, **64**, 149 (1964).

(7) W. von E. Doering and R. A. Odum, *Tetrahedron*, **22**, 81 (1966).

(8) R. Huisgen, D. Vossins, and M. Appl, *Chem. Ber.*, **91**, 1 (1958).

(9) The nmr, infrared, and ultraviolet spectra are identical with those reported for the compound prepared by photolysis of phenyl azide in diethylamine.[7]

(10) Analysis of the crude liquid fraction from the amine reactions by gas chromatography always revealed small quantities of aniline. In one case, dimethylamine, N′,N′-dimethyl-N-phenylhydrazine was also present as a minor constituent. This hydrazine along with aniline are products amounting to a few per cent from the photolysis of phenyl azide in dimethylamine.

(11) All nmr spectra were determined with a Varian A-60 spectrometer using tetramethylsilane as an internal standard. Multiplets for all of the five types of ring protons are centered within these ranges.

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Some Novel Features in the Mass Spectra of Polynuclear Metal Carbonyl Derivatives[1]

Sir:

The positive ion mass spectra of numerous metal carbonyl derivatives are presently being studied in this laboratory.[2] Some preliminary results are now being reported in several areas of special significance regarding both metal–metal bonding and the nature of some unusual olefin complexes of iron carbonyl.

I. "Bare" Metal Cluster Ions. The tendency for metal carbonyls containing no other ligands to lose carbonyl groups stepwise upon electron bombardment in the mass spectrometer has been demonstrated for the mononuclear derivatives $M(CO)_x$ (x = 6, M = Cr, Mo, or W;[3,4] x = 5, M = Fe;[4,5] x = 4, M = Ni[5]) and the binuclear derivatives $Co_2(CO)_8$ and $Mn_2(CO)_{10}$.[6] Extension of this effect has now resulted in the observa-

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(1) The author is indebted to the National Science Foundation for partial support of this work under Grant GP-3954.

(2) The mass spectra reported in this communication were taken at 70-ev electron energies on an Associated Electrical Industries MS-9 mass spectrometer. The author is indebted to Mr. R. E. Rhodes for taking the mass spectra.

(3) R. E. Winters and R. W. Kiser, *Inorg. Chem.*, **4**, 157 (1965).

(4) A. Foffani, S. Pignataro, B. Cantone, and F. Grasso, *Z. Physik. Chem.* (Frankfurt), **45**, 79 (1965).

(5) R. E. Winters and R. W. Kiser, *Inorg. Chem.*, **3**, 699 (1964).

(6) R. E. Winters and R. W. Kiser, *J. Phys. Chem.*, **69**, 1618 (1965).

tion of metal cluster ions containing no other ligands in the mass spectra of certain tri- and tetranuclear metal carbonyls.

The mass spectrum of $Co_4(CO)_{12}$ provides the clearest example of this effect because natural cobalt is monoisotopic. Besides the ions $Co_4(CO)_n^+$ $(1 < n \leq 12)$, the Co_4^+ ion (*m/e* 236) is observed. The tetrahedral[7] configuration of the four cobalt atoms in $Co_4(CO)_{12}$ suggests that this Co_4^+ ion might be a tetrahedral cluster of four "bare" cobalt atoms.

The mass spectrum of $Ru_3(CO)_{12}$ is entirely analogous but complicated by the presence of seven stable isotopes[8] in natural ruthenium. All possible $Ru_3(CO)_n^+$ $(1 < n < 12)$ ions are observed. However, the Ru_3^+ ion was also observed. The triangular structure[9] established for $Ru_3(CO)_{12}$ suggests a triangular configuration of ruthenium atoms in the Ru_3^+ ion.

The mass spectrum of $Fe_3(CO)_{12}$ is somewhat different.[10] Stepwise loss of carbonyl groups as far as $Fe_3(CO)_3^+$ is observed. However, further degradation, even from the $Fe_3(CO)_4^+$ stage, appears to take place by rupture of iron–iron bonds producing iron carbonyl fragments such as $Fe_2(CO)_4^+$, $Fe_2(CO)_3^+$, $Fe(CO)_4^+$, $Fe(CO)_3^+$, $Fe(CO)_2^+$, and $FeCO^+$. The metal–metal bonds in $Fe_3(CO)_{12}$ appear to be weaker relative to the metal–carbonyl bonds than the metal–metal bonds in $Ru_3(CO)_{12}$.

Mass spectra of the compounds $YCCo_3(CO)_9$ (Y = CH_3 and Cl) were also investigated. In both cases stepwise loss of the nine carbonyl groups was observed resulting in $YCCo_3^+$ fragments.

The structures of $YCCo_3(CO)_9$ compounds[11] suggest that these $YCCo_3^+$ ions have a trigonal pyramidal (*i.e.*, irregular tetrahedral) structure with three cobalt atoms at the base and a carbon atom at the apex.

These studies thus provide a dramatic illustration of the high stability of metal–metal bonds relative to metal–carbonyl bonds in many polynuclear metal carbonyl derivatives. Further studies to observe unusual "bare" metal cluster ions in the mass spectrometer are being made as appropriate substances become available.

II. The Chromium–Chromium Bond in $[C_5H_5Cr(CO)_3]_2$. Fischer and Hafner[12] first prepared the dark green chromium complex $[C_5H_5Cr(CO)_3]_2$. They formulated it as the dimer on the basis of its diamagnetism and its molecular weight in benzene solution. The close relationship of dimeric $[C_5H_5Cr(CO)_3]_2$ to the monomeric $V(CO)_6$ and the much lower sublimation temperature of $[C_5H_5Cr(CO)_3]_2$ (~100° at 0.1 mm) relative to its molybdenum analog $[C_5H_5Mo(CO)_3]_2$ (~150° at 0.1 mm) suggested the possibility of dissociation of dimeric $[C_5H_5Cr(CO)_3]_2$ to monomeric $C_5H_5Cr(CO)_3$.[13,14]

The mass spectrum of a sample of dark green $[C_5H_5Cr(CO)_3]_2$ exhibited no ions containing two chromium atoms. The ions $C_5H_5Cr(CO)_3^+$ (*m/e* 201) and $C_5H_5Cr(CO)_3H^+$ (*m/e* 202) were the highest mass ions in the mass spectrum. By contrast, the mass spectrum of the molybdenum analog $[C_5H_5Mo(CO)_3]_2$ exhibited the ions $(C_5H_5)_2Mo_2(CO)_x^+$ (x = 0, 2, 3, 4, 5, and 6).

These mass spectral data indicate that the chromium–chromium bond in $[C_5H_5Cr(CO)_3]_2$ is so weak that it breaks upon vaporization to give monomeric $C_5H_5Cr(CO)_3$ vapor. By contrast, the molybdenum–molybdenum bond in $[C_5H_5Mo(CO)_3]_2$ remains intact on vaporization. This difference in the stability of the metal–metal bonds in the chromium and molybdenum compounds of the type $[C_5H_5M(CO)_3]_2$ also accounts for the greater reactivity of $[C_5H_5Cr(CO)_3]_2$ to hydrogen[12] and nitric oxide.[15] Further studies on $[C_5H_5Cr(CO)_3]_2$ and related compounds are in progress to clarify this phenomenon.

III. The Nature of Some Novel Olefin Complexes of Iron Carbonyl. The number of carbonyl groups in complex olefin derivatives of metal carbonyls is often difficult to establish unequivocally by chemical analyses. The stepwise fragmentation of metal carbonyl groups in the mass spectra of such compounds makes possible their unequivocal formulation by mass spectroscopy. Two examples where mass spectroscopy indicates the literature formulation to require revision and two examples of new and unusual compounds discovered by mass spectroscopy are cited briefly.

By reaction between $Fe_3(CO)_{12}$, 1,4-dibromobutyne, and zinc, Nakamura, Kim, and Hagihara[16] obtained the red-orange butatriene complex, mp 69–70°, which they formulated as the diiron pentacarbonyl $C_4H_4Fe_2(CO)_5$. They also reported further studies on related compounds.[17] The mass spectrum of this compound exhibited not only the ions $C_4H_4Fe_2(CO)_x^+$ $(0 \leq x \leq 5)$ but also the ion $C_4H_4Fe_2(CO)_6^+$ (*m/e* 332). Correct formulation of this complex thus appears to be the diiron hexacarbonyl $C_4H_4Fe_2(CO)_6$.[18]

Reaction between $Fe_3(CO)_{12}$ and acenaphthylene gives a red-violet solid previously[19] formulated as the diiron hexacarbonyl $C_{12}H_8Fe_2(CO)_6$. However, the highest mass ion in the mass spectrum of this complex[20] is $C_{12}H_8Fe_2(CO)_5^+$ (*m/e* 404) indicating this acenaphthylene complex to be the diiron pentacarbonyl $C_{12}H_8Fe_2(CO)_5$.

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[7] P. Corradini, *J. Chem. Phys.*, 31, 1676 (1959).

[8] The following isotopes compose natural ruthenium: ^{96}Ru (5.51%), ^{98}Ru (1.87%), ^{99}Ru (12.72%), ^{100}Ru (12.62%), ^{100}Ru (17.07%), ^{102}Ru (31.63%), and ^{104}Ru (18.58%) [A. E. Cameron and E. Wichers, *J. Am. Chem. Soc.*, 84, 4175 (1962)].

[9] E. R. Corey and L. F. Dahl, *Inorg. Chem.*, **1**, 521 (1962).

[10] A complicating factor in the mass spectrum of polynuclear iron carbonyl derivatives is the closeness of the mass of the most common iron isotope, ^{56}Fe, and that of two carbonyl groups. Assignments of molecular formulas to the observed ions in the $Fe_3(CO)_{12}$ mass spectrum are aided by comparison of the relative abundances of neighboring ions to those expected from the natural abundance of iron (and to a less extent carbon and oxygen) isotopes.

[11] For a brief summary of the chemistry of the $YCCo_3(CO)_9$ compounds, see R. B. King, *Advan. Organometal. Chem.*, 2, 243 (1964).

[12] E. O. Fischer and W. Hafner, *Z. Naturforsch.*, **10b**, 140 (1955); E. O. Fischer, W. Hafner, and H. O. Stahl, *Z. Anorg. Allgem. Chem.*, **282**, 47 (1955); R. B. King and F. G. A. Stone, *Inorg. Syn.*, 7, 104 (1963).

[13] Recent esr studies by Keller and Wawersik[14] have demonstrated the tendency for the binuclear $Co_2(CO)_8$ to dissociate on vaporization to give monomeric $Co(CO)_4$ free radicals.

[14] H. J. Keller and H. Wawersik, *Z. Naturforsch.*, **20b**, 938 (1965).

[15] E. O. Fischer, O. Beckert, W. Hafner, and H. O. Stahl. *ibid.*, **10b**, 598 (1955).

[16] A. Nakamura. P. J. Kim, and N. Hagihara, *J. Organometal. Chem.* (Amsterdam), **3**, 7 (1965).

[17] A. Nakarmura, *Bull. Chem. Soc. Japan*, **38**, 1868 (1965).

[18] The diiron hexacarbonyl formulation for the analogous tetraphenylbutatriene derivative, $(C_6H_5)_4C_4Fe_2(CO)_6$, has been confirmed by unpublished X-ray crystal structure data presented by O. S. Mills at the Second International Symposium on Organometallic Chemistry, Madison, Wis., Sept 1, 1965. Unpublished Mössbauer data (R. B. King and L. M. Epstein) indicate the presence of only one type of iron atom in the butatriene–iron carbonyl complex. also supporting formulation as the hexacarbonyl, $C_4H_4Fe_2(CO)_6$, rather than the pentacarbonyl.

[19] R. B. King and F. G. A. Stone, *J. Am. Chem. Soc.*, **82**, 4557 (1960).

[20] The sample used for this study was purified by careful slow vacuum sublimation at 100° (0.1 mm). Slight overheating to ~120° leads to decomposition producing acenaphthylene.

Acenaphthylene thus behaves like azulene in forming a diiron pentacarbonyl complex. The formulation of the deep red azulene complex $C_{10}H_8Fe_2(CO)_5$ prepared by Burton, Pratt, and Wilkinson[21] from azulene and iron pentacarbonyl has been confirmed by mass spectroscopy. However, reaction between azulene and iron pentacarbonyl under slightly different conditions results in a different dark red complex indicated by mass spectroscopy to be $[C_{10}H_8Fe(CO)_2]_2$, apparently closely related to $[C_{10}H_8Mn(CO)_3]_2$[21] and $[C_{10}H_8V(CO)_4]_2$.[22]

A volatile yellow solid, mp 113–115°, obtained from $Fe_3(CO)_{12}$ and allene dimer, C_6H_8 (mixture of ~80% 1,2-dimethylenecyclobutane and ~20% 1,3-dimethylenecyclobutane), has now been shown to be the dicarbonyl $C_{12}H_{16}Fe(CO)_2$ by its mass spectrum. Although infrared and nmr spectra of this unusual, very rare complex are available, an unequivocal decision cannot yet be made between any of several possible structures.

Details of the mass spectra of these olefin complexes of iron carbonyl will be included in future publications on their synthesis and properties.

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[21] R. Burton, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 4290 (1960).

[22] E. O. Fischer, Abstracts of Papers presented at the Symposium on Current Trends in Organometallic Chemistry, Cincinnati, Ohio, June 1963, p 66.

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Nitrogen-15 Nuclear Magnetic Resonance Evidence That Mg^{2+} Does Not Complex with Nitrogen Atoms of Adenosine Triphosphate

Sir:

Because Mg^{2+} cocatalyzes with ATPases, and because ITP and ATP are enzymatically nonequivalent, it is reasonable to guess that Mg^{2+} interacts with the ring moiety of ATP and other nucleoside triphosphates; if so, then, in a solution containing only Mg^{2+} and ATP, an internal chelate (Mg^{2+} interacting simultaneously with ring N atoms and triphosphate O atoms) might result.[1] One of us[2] has previously taken ultraviolet difference spectra to support this idea. Recent studies[3] have concluded, however, that this structure does not form. The most persuasive of these studies have employed nuclear magnetic resonance (nmr), but have thus far been indirect in that the resonances studied were those of protons bonded to C atoms, not those of the N atoms which would be primarily involved. In the present work, by using ^{15}N-substituted ATP, we have succeeded in studying the N resonances, and conclude that Mg^{2+} does not interact with these atoms whereas Zn^{2+} does.

The ^{15}N nmr spectra were obtained at a frequency of about 6.053 Mcps and a magnetic field of 14,025 gauss by the frequency sweep method using a Hewlett Packard Model 5100A frequency synthesizer. A Nuclear Data Model ND-160 Enhancetron was used to enhance signal-to-noise ratios by making repetitive scans of the spectrum.[4] The frequency sweep was derived from the analyzer sweep so that chemical shifts could be measured by counting the frequency synthesizer output frequency at a particular channel containing an nmr peak maximum.

The ATP used for these experiments was 70% enriched in ^{15}N at all nitrogen positions. The nmr samples were 0.5–0.9 *M* in ATP. When samples containing metal ions were prepared, $ZnCl_2$ or $MgCl_2$ was added in amounts needed to give equal metal ion and ATP concentrations. Sample pH was adjusted to about 9.5 with NaOH. Under these conditions the hypothetical metal ion–adenine ring interaction should have been about 90% saturated even for an association constant as low as 1×10^2. Deuterium was usually substituted for exchangeable protons in the sample by lyophilization and solution in D_2O steps. Sample temperature during the measurements was 34°. Chemical shifts did not change noticeably over the pH range 7.0 to 9.6.

Five well-separated nitrogen resonances were observed. These were assigned to particular nitrogen atoms of ATP on the basis of (1) fine structure due to spin–spin coupling interactions, (2) behavior in H_2O and in D_2O solution, and (3) reported values of ^{14}N chemical shifts.

The peak at highest field was assigned to the 6-amino nitrogen.[5] It could only be detected in D_2O solution. Incomplete collapse of the nitrogen–proton spin–spin coupling interaction severely broadened the resonance in H_2O solution. The N-9 resonance could be identified because it was a single line. This nitrogen is not part of a conjugated system and should not couple strongly to nearby protons. The remaining three nitrogen resonances were doublets due to spin–spin coupling to protons on adjacent carbon atoms; N-7 exhibited a 10-cps coupling to H-8 and occurred at lowest field; N-1 and N-3 couple equally to H-2 with $J = 16$ cps. On the basis of Herbison-Evans' and Richards'[6] measurements of ^{14}N chemical shifts in NH_2-substituted pyridine, N-1 should be found at a higher field than N-3. The 10-ppm shift observed between these two nitrogens of ATP is equal to the separation between the heterocyclic nitrogens of *o*- and *p*-amino-substituted pyridines. Chemical shifts for the five nitrogen atoms of ATP are given in Table I. The shifts are also given for ATP in the presence of Mg^{2+} and Zn^{2+} ions.

The results show that there is no significant shift in any nitrogen peak when Mg^{2+} is added to ATP. If Mg^{2+} had coordinated with a nitrogen of the adenine

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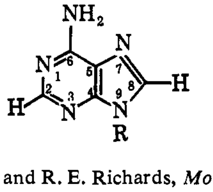
[1] A. Szent-Györgyi, "Enzymes. Units of Biological Structure and Function," O. H. Gaebler, Ed., Academic Press Inc., New York, N. Y., 1956, p 393.

[2] K. Hotta, J. Brahms, and M. Morales, *J. Am. Chem. Soc.*, **83**, 997 (1961).

[3] (a) P. W. Schneider, H. Brintzinger, and H. Erlenmeyer, *Helv. Chim. Acta*, 47, 992 (1964); (b) M. Cohn and T. R. Hughes, Jr., *J. Biol. Chem.*, **237**, 176 (1962); (c) G. G. Hammes, G. E. Maciel, and J. S. Waugh, *J. Am. Chem. Soc.*, **83**, 2394 (1961).

[4] M. P. Klein and G. W. Barton, Jr., *Rev. Sci. Instr.*, **34**, 754 (1963).

[5] The adenine ring portion of ATP is numbered as follows.



[6] D. Herbison-Evans and R. E. Richards, *Mol. Phys.*, **7**, 19 (1964).