isomer (2.533 Å),[3,18] in the transoid [Fe(h^5-C$_5$H$_5$)(CO)$_2$]$_2$ isomer (2.49 (2) Å),[4,18] in the cisoid [Fe(h^5-C$_5$H$_5$)(CO)-(COAl(C$_2$H$_5$)$_3$)]$_2$ adduct (2.49 (1) Å),[5,18] in the acetylenic diphosphine derivative [Fe$_2$(h^5-C$_5$H$_5$)$_2$(CO)$_3$]$_2$[(C$_6$H$_5$)$_2$-PC$_2$P(C$_6$H$_5$)$_2$] (2.54 Å),[6,18] and in the cisoid [Fe$_2$-(h^5-C$_5$H$_5$)$_2$(CO)$_3$(CNC$_6$H$_5$)] isomer (2.53 Å).[7,18] Expectedly, the Fe–Fe bond length is also longer and the bridging Fe–S–Fe angles are larger in the cation than those in the dimercapto-bridged [Fe(CO)$_3$(SC$_2$H$_5$)]$_2$ dimer (2.54 (1) Å, 68°),[8] in the dimercapto-bridged [Fe(NO)$_2$(SC$_2$H$_5$)]$_2$ dimer (2.720 (3) Å, 74°),[9] and in the dimercapto- and dithioxanthate-bridged [Fe(S$_2$CSC$_2$-H$_5$)$_2$(SC$_2$H$_5$)]$_2$ dimer (2.61 (1) Å; bridging mercapto ligands, 72°).[10] In each of these above molecules a two-electron iron–iron bond is in accord with the observed diamagnetism.

This study thereby provides an operational test of our hypothesis (which motivated this research) that one may expect a dramatic decrease in the metal–metal distance of a dimeric complex containing no electron-pair metal–metal bond to a value intermediate between that of a "no bond" distance and a two-electron bond distance if the electron is removed from an MO which is *strongly* antibonding with respect to the two metal atoms. Hence from a qualitative viewpoint the [Fe(h^5-C$_5$H$_5$)(CO)(SR)]$_2^+$ cation may simply be regarded as having *two* electrons in a *bonding* metal σ orbital combination and *one* electron in the corresponding antibonding combination. The resulting net metal–metal bond order (based on the Coulson definition[19]) is thereby 0.5, which, in valence-bond terminology, corresponds to a *one-electron metal–metal bond.*[20]

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(18) The two crystalline isomers[3,4] of [Fe(h^5-C$_5$H$_5$)(CO)$_2$]$_2$ are cisoid and transoid with respect to the two terminal carbonyl groups (and two cyclopentadienyl rings). The [Fe(h^5-C$_5$H$_5$)(CO)(COAl(C$_2$H$_5$)$_3$)]$_2$ complex,[5] an aluminum triethyl adduct of [Fe(h^5-C$_5$H$_5$)(CO)$_2$]$_2$, has the two terminal carbonyl groups in a cisoid arrangement with an Al(C$_2$H$_5$)$_3$ coordinated to each of the two bridging carbonyl oxygen atoms. The [Fe$_2$(h^5-C$_5$H$_5$)$_2$(CO)$_3$]$_2$[(C$_6$H$_3$)$_2$PC$_2$P(C$_6$H$_5$)$_2$] molecule[6] consists of two identical Fe$_2$(h^5-C$_5$H$_5$)$_2$(CO)$_3$ moieties each linked to a different phosphorus atom of the bridging (C$_6$H$_5$)$_2$PC$_2$P(C$_6$H$_5$)$_2$ ligand such as to give molecular symmetry C_i-1; the phosphorus atom and one terminal carbonyl group of each Fe$_2$(h^5-C$_5$H$_5$)$_2$(CO)$_3$P fragment are cisoid. The Fe$_2$(h^5-C$_5$H$_5$)$_2$(CO)$_3$(CNC$_6$H$_5$) isomer[7] possesses a cisoid orientation of two terminal carbonyl groups with one bridging carbonyl and one bridging isonitrile group. Each of these above five complexes, which differ in constitution from the [Fe(h^5-C$_5$H$_5$)(CO)(SR)]$_2$ dimer by the replacement of the bridging mercapto three-electron donors with carbon-bridging two-electron donors (*viz.*, bridging CO, COAl(C$_2$H$_5$)$_3$, or isonitrile ligands), requires a two-electron Fe–Fe bond in order for each iron atom to achieve a closed-shell electronic configuration.

(19) C. A. Coulson, *Proc. Chem. Soc., Ser. A,* **169**, 413 (1938).

(20) It is noteworthy that the corresponding monocharged [Mn-(h^5-C$_5$H$_5$)(CO)(SR)]$_2^-$ anion is isoelectronic with the [Fe(h^5-C$_5$H$_5$)(CO)-(SR)]$_2^+$ cation. Detailed stereochemical comparisons of these and other isoelectronic cations and anions are needed to give further insight concerning the correlation of the observed molecular features with electronic bonding models.

* Address correspondence to this author.

Neil G. Connelly, Lawrence F. Dahl*

*Department of Chemistry, University of Wisconsin
Madison, Wisconsin 53706*
Received September 8, 1970

The Mechanism of the Reaction of 4-Picoline N-Oxide with Acetic Anhydride Studied by Nuclear Magnetic Resonance Spectroscopy

Sir:

Attempts to delineate the mechanism of the reaction between 4-picoline N-oxide (1) and acetic anhydride have so far not been completely successful.[1] According to the recent tracer studies utilizing ^{18}O-labeled acetic anhydride,[2] it appears almost conclusive that in the absence of solvents or in acetic acid, 4-acetoxymethylpyridine (2) and 3-acetoxy-4-methylpyridine (3) are formed by intermolecular rearrangement with nucleophilic attack of an acetate anion on the intermediate anhydro base 4, as originally suggested by Berson and Cohen.[3] With the use of an equimolar amount of acetic anhydride in tenfold molar amounts of aromatic solvents, however, results were obtained which suggest operation of the predominantly intramolecular radical-pair process.[4] More recently, similar ester-forming rearrangement encountered in the reaction of 1 with phenylacetic anhydride was considered to indicate the nonradical paths,[5] because a phenylacetoxyl radical is even less stable than the exceedingly unstable acetoxyl radical and it is extremely unlikely that the former is capable of existence.[6] Cohen and Deets claimed further to have demonstrated the ionic mechanism by trapping the cationic intermediates in anisole and benzonitrile.[7]
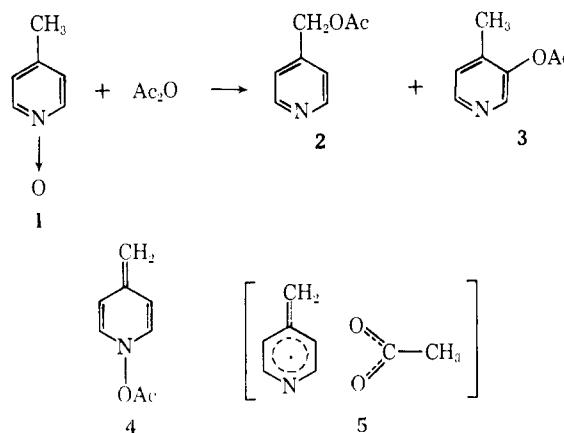
In this communication we report the observation of the chemically induced nuclear spin polarization during the reaction of 1 with acetic anhydride to give direct evidence for the radical pair 5.[8]

(1) H. J. Shine, "Aromatic Rearrangements," Elsevier, Amsterdam, 1967, p 284; E. Ochiai, "Aromatic Amine N-Oxides," Elsevier, Amsterdam, 1967; A. R. Katritzky, *Quart. Rev., Chem. Soc.,* **10**, 395 (1956).
(2) S. Oae, T. Kitao, and Y. Kitaoka, *J. Amer. Chem. Soc.,* **84**, 3362 (1962).
(3) J. A. Berson and T. Cohen, *ibid.,* **77**, 1281 (1955).
(4) S. Oae, Y. Kitaoka, and T. Kitao, *Tetrahedron,* **20**, 2685 (1964); V. J. Traynelis and A. I. Gallagher, *J. Amer. Chem. Soc.,* **87**, 5710 (1965).
(5) T. Cohen and J. H. Fager, *ibid.,* **87**, 5701 (1965).
(6) M. Szwarc, "Peroxide Reaction Mechanisms," J. O. Edwards, Ed., Wiley-Interscience, New York, N. Y., 1962, p 156; L. Herk, M. Feld, and M. Swarc, *J. Amer. Chem. Soc.,* **83**, 2998 (1961); T. C. Vogt and W. H. Hamill, *J. Phys. Chem.,* **67**, 292 (1963); M. J. Goldstein, *Tetrahedron Lett.,* 1601 (1964).
(7) T. Cohen and G. L. Deets, *J. Amer. Chem. Soc.,* **89**, 3939 (1967).
(8) For a brief review, see H. Fischer and J. Bargon, *Accounts Chem. Res.,* **2**, 110 (1969). More recent works: G. L. Closs, *J. Amer. Chem. Soc.,* **91**, 4552 (1969); G. L. Closs and A. D. Trifunac, *ibid.,* **91**, 4554 (1969); G. L. Closs and L. E. Closs, *ibid.,* **91**, 4549 (1969); G. L. Closs and A. D. Trifunac, *ibid.,* **92**, 2183 (1970); G. L. Closs, C. E. Double-
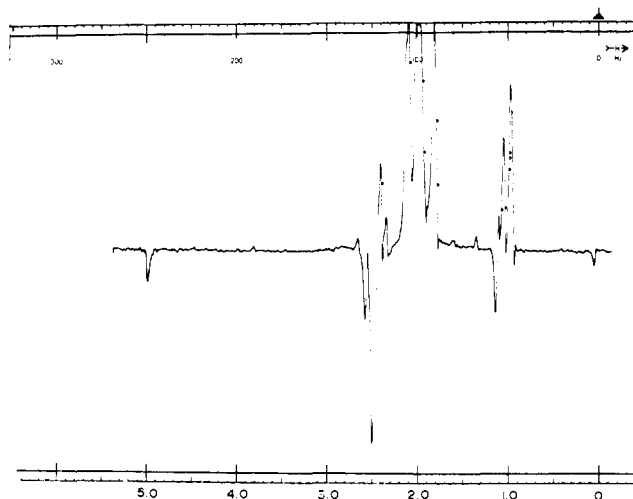
Figure 1. 100-MHz nmr spectrum of a solution of **1** and acetic anhydride in benzene at 95°. The scanning of the spectrum was started toward the higher field at 35 sec after insertion of the sample to the nmr cavity with a sweep rate of 100 sec/1000 Hz.

Figure 2. Plot of signal intensities *vs.* reaction time: (a) the singlet at 4.89 ppm; (b) the triplet-quartet signals of 4-ethylpyridine.

In a typical run, 130 mg of 4-picoline *N*-oxide (**1**) and 300 μl of acetic anhydride were dissolved in 100 μl of benzene which served as the internal lock and as the diluent of the reaction, degassed and sealed in an nmr sample tube. In 20 sec after insertion of the sample into the nmr cavity, which had been heated at 95°, of a Varian HA 100 D spectrometer, there appeared the emission (abbreviated as E) and enhanced absorption (A) signals at δ 4.98 (E), 2.58 (E), 2.50 (E) 2.42 (A), 2.35 (A), 1.14 (E), 1.06 (A), 0.97 (A), and 0.05 (E) ppm relative to the internal tetramethylsilane (Figure 1). The intensity of the emission singlet at 4.98 ppm reached a maximum at *ca.* 75 sec and decayed to an apparent zero in 115 sec as shown in Figure 2a, while those of the multiplets in the higher field reached their maxima irrespective of the sign at *ca.* 100 sec at the reaction temperature of 75° (Figure 2b).

By comparison with the spectra of the authentic samples, the emission singlet at δ 4.98 ppm was found to be due to the methylene protons of **2**. The skewed quartet centering at 2.46 and the triplet at 1.06 ppm obtained above were superimposable with the ethyl signals of 4-ethylpyridine with respect to the chemical shifts.[9] The origin of the 0.05-ppm emission was identified as methane.

Thus direct evidence in favor of the intermediacy of free radicals in formation of **2** as well as 4-ethylpyridine and methane has now been obtained.[10] It is noticed,

day, and D. R. Paulson, *J. Amer. Chem. Soc.*, **92**, 2185 (1970); G. L. Closs and A. D. Trifunac, *ibid.*, **92**, 2186 (1970); A. R. Lepley, P. M. Cook, and G. F. Willard, *ibid.*, **92**, 1101 (1970); M. Cocivera and A. M. Trozzolo, *ibid.*, **92**, 1772 (1970); R. Kaptein and L. J. Oosterhoff, *Chem. Phys. Lett.*, **4**, 195, 214 (1969); H. R. Ward, R. G. Lawler, H. Y. Loken, and R. A. Cooper, *J. Amer. Chem. Soc.*, **91**, 4928 (1969); J. E. Baldwin and J. E. Brown, *ibid.*, **91**, 3647 (1969); J. E. Baldwin, W. F. Erickson, R. E. Hackler, and R. M. Scott, *Chem. Commun.*, 576 (1970); R. W. Jemison and D. G. Morris, *ibid.*, 1226 (1969); D. G. Morris, *ibid.*, 1345 (1969); S. F. Nelsen, R. B. Metzler, and M. Iwamura, *J. Amer. Chem. Soc.*, **91**, 5103 (1969); H. Iwamura, M. Iwamura, T. Nishida and I. Miura, *Bull. Chem. Soc. Jap.*, **43**, 1914 (1970).

(9) Formation of 4-ethylpyridine as the by-product of the rearrangement in 1.6–2.0% yield was also confirmed by vpc.[1]

(10) A referee suggested several possibilities in which none of the reaction to give **2** proceeds by a radical pair **5**: (1) a picolyl radical may abstract an acetoxy radical from **4** as a minor route; (2) the product **2** may dissociate and recombine slightly at the reaction temperature (*cf.* J. Jacobus, *Chem. Commun.*, 709 (1970)); or (3) the emission may be
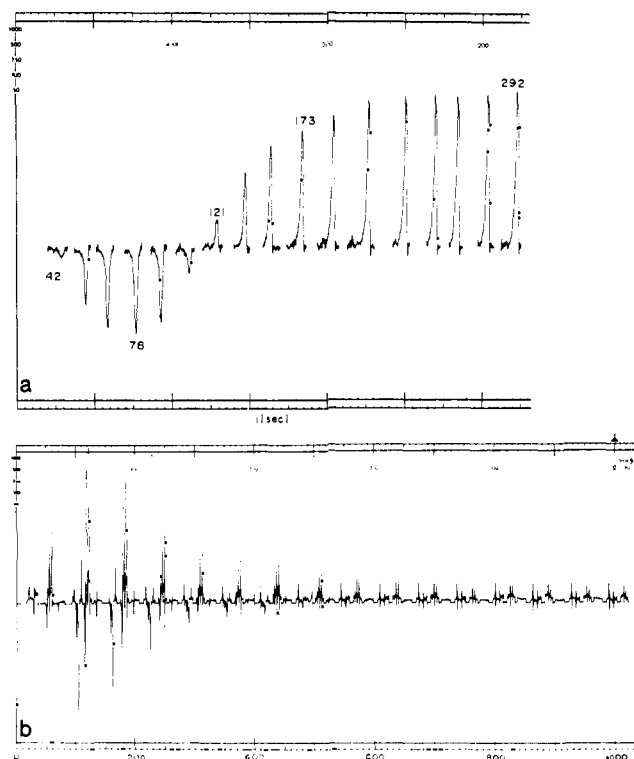
however, that the apparent enhancement factor of the nuclear polarization in **2** is considerably smaller than that of 4-ethylpyridine. By assuming the first-order kinetic law for formation of these two products, the maximum enhancement factors of 3 and 10^2 were obtained. The smaller value in the former might somehow be due to shorter spin–lattice relaxation time of the methylene protons in **2**. This possibility was ruled out when it was found by the method of adiabatic rapid passage through resonance[11] that T_1's were 7.2, 10.4, and 10.0 sec for the methylene protons of **2** and the methyl and methylene protons of 4-ethylpyridine, respectively. The difference cannot be enough to explain the large difference in polarization factors. Although there is no *a priori* reason why the magnitude of polarization should be comparable,[12] it may be more

coming from a trace product other than **2**. The steady-state concentration of **4** under the reaction condition is expected to be low (*cf.* V. J. Traynelis and P. L. Pacini, *J. Amer. Chem. Soc.*, **86**, 4917 (1964), for the anhydro base of 2-picoline *N*-oxide), and, for case 1 to occur, the specific rate of the reaction has to be extremely high. It is unlikely that case 1 is responsible for all of the polarization in **2**. In a separate run, a solution of the authentic sample of **2** was heated under the experimental conditions for 5 hr. As far as the sensitivity of the nmr spectrum was concerned, the ester **2** was definitely stable and no trace of a new peak was observed to appear. If there were a slight dissociation of **2** into the radical pair **5**, there would have been a chance for the acetoxy radical to decarboxylate, and 4-ethylpyridine and methane must have been accumulated at least in a trace amount. Without benzene as a diluent of the reaction, and also in *o*-dichlorobenzene instead of benzene, an emission signal was observed exactly where the methylene protons of **2** appeared. It is a rather remote possibility that a trace product other than **2** has exactly the same chemical shift in reasonably different solvent systems.

(11) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, N. Y., 1959, p 83.

(12) According to the mechanism proposed by Closs[8] which ascribes the nuclear spin polarization to the singlet–triplet mixing in the radical pair by *g* shift and hyperfine coupling, smaller polarization in absolute

reasonable to consider the difference to indicate that only a fraction of the ester product 2 is attributed to radical-pair recombination. Thus together with the already established ^{18}O scrambling, intramolecularity of rearrangement in aromatic solvents,[4] and rate-determining deprotonation mechanism,[13] the present findings are compatible with a dual mechanism[1,4,14] in which the anhydro base 4 cleaves to both radical and ion pairs. The ester product 2 can result from both but only the radical manifold should give polarization.

value could be expected among other possible combinations of the two magnetic parameters when a radical pair has accidentally almost equal g values. In comparison with the carbon radicals which have g values close to those of the free electrons, the oxygen radicals usually have larger g factors due to larger spin-orbit coupling. The radical pair leading to 4-ethylpyridine is composed of two carbon radicals while a carbon and an oxygen radical constitute the pair 5. Therefore, it is the radical pair 5 which is expected to have a larger g shift and, consequently larger enhancement. On the other hand, when the lifetime of 5 is assumed to be shorter than that of the methyl-4-picolyl pair, it then follows that the former should have smaller polarization. In view of the relative stability of acetoxy compared with methyl radicals,[6] there could be a reasonable difference in lifetime in the vicinity of the inverse of the diffusion-controlled rate.

(13) S. Oae, S. Tamagaki, T. Negoro, K. Ogino, and S. Kozuka, *Tetrahedron Lett.*, 917 (1968).
(14) V. J. Traynelis and R. F. Martello, *J. Amer. Chem. Soc.*, 82, 2744 (1960).
* Address correspondence to this author.

Hiizu Iwamura*
Department of Chemistry, Faculty of Science
The University of Tokyo, Bunkyo-ku, Tokyo, Japan

Michiko Iwamura
Department of Chemistry, Faculty of Science
Toho University, Narashino-shi, Japan

Toshiaki Nishida, Shiro Sato
Application Laboratory
Nippon Electric Varian, Limited, Azabu, Tokyo, Japan

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σ–π Conjugation of Carbon–Metal Bonds. Stereoelectronic and Inductive Effects[1,2]

Sir:

A variety of chemical[3a,4,5] and spectroscopic[3b,f,6] evidence indicates that carbon–metal bonds stabilize

(1) Supported by the Air Force Office of Scientific Research, Grant No. AFOSR-69-1639.
(2) Presented in part at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968, p 39. Previous papers in this series are given in ref 3.
(3) (a) J. C. Ware and T. G. Traylor, *Tetrahedron Lett.*, 1295 (1965); (b) T. G. Traylor and J. C. Ware, *J. Amer. Chem. Soc.*, 89, 2304 (1967); (c) T. T. Tidwell and T. G. Traylor, *ibid.*, 88, 3442 (1966); (d) W. Hanstein and T. G. Traylor, *Tetrahedron Lett.*, 4451 (1967); (e) J. A. Mangravite and T. G. Traylor, *ibid.*, 4457 (1967); (f) W. Hanstein, H. J. Berwin, and T. G. Traylor, *J. Amer. Chem. Soc.*, 92, 829 (1970); (g) a general theory for exalted hyperconjugation of polarized,[3b] bent,[3h] stretched, or otherwise weakened σ bonds will be presented in a forthcoming paper; (h) Nye A. Clinton, R. S. Brown, and T. G. Traylor, *J. Amer. Chem. Soc.*, 92, 5228 (1970).
(4) A. N. Nesmeyanov and I. I. Kritskaya, *Dokl. Akad. Nauk. SSSR*, 121, 447 (1958).
(5) Yu. G. Bundel, N.-D. Antonova, and A. O. Reutov, *ibid.*, 166, 1103 (1966).
(6) (a) The ultraviolet spectra of A and B reported by Petrukov, Mironov, and Shorygin[6b] agree with this postulate. However, because uv transitions involve two orbitals, both having energies dependent upon

A, <180 nm   B, 226 nm
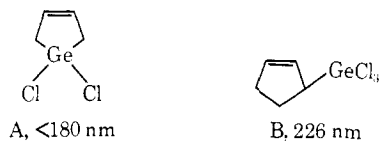
structural changes, these data have not been generally accepted as proof of σ–π conjugation.[7] Thus allyl or benzyl metal compounds are usually

neighboring cationic centers by (vertical)[3f,g] σ–π conjugation (I) rather than neighboring nucleophilic participation (II). It has been suggested[3b,4] that σ–π
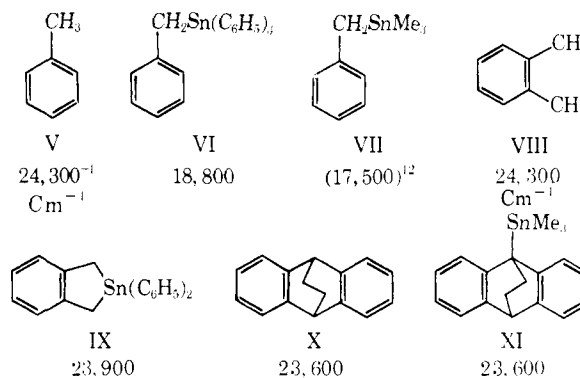
I   II
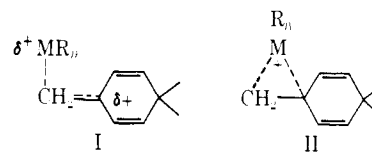
conjugation, like all other types of π conjugation, requires coplanarity of the C–M bond and the axis of the electron-deficient π orbital (or p orbital) as in III or IV.

III   IV
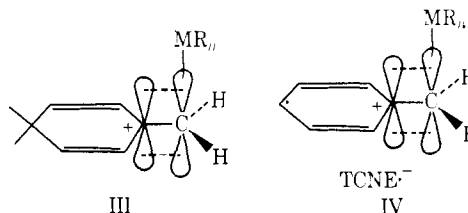
We report here charge-transfer spectra which permit the separation of the large stereoelectronic effects of the $C–MR_n$ σ bond from the very small inductive effects of the $–MR_n$ group. The effects of changes in R upon the σ–π conjugation of MR_n are also reported.

Charge-transfer frequencies of the organometallic compounds shown below with tetracyanoethylene were observed in methylene chloride solution as previously described.[3f] The frequencies are listed under each structure.[11]

V   VI   VII   VIII

24,300⁻¹   18,800   (17,500)[12]   24,300
Cm⁻¹   Cm⁻¹
                                         SnMe₃

IX   X   XI
23,900   23,600   23,600

In order to appreciate the enormous stabilization provided to cations by the $–CH_2Sn(C_6H_5)_3$ and $–CH_2$-

discussed in terms of inductive effects[9] or dπ–pπ interactions[10] (*e.g.*, II). (b) V. A. Petrukov, V. F. Mironov, and P. P. Shorygin, *Izv. Akad. Nauk. SSSR, Ser. Khim.*, 12, 2203 (1964); (c) P. P. Shorygin, V. A. Petrukov, and L. C. Stalyarova, *Dokl. Akad. Nauk. SSSR*, 154, 441 (1964); (d) N. S. Nametkin, V. M. V'dovin, E. Sh. Finkelstein, T. N. Arkhipova, and V. D. Oppenheim, *ibid.*, 154, 383 (1964).
(7) Similar difficulties have plagued the spectroscopic studies of conjugation with the cyclopropyl group.[8]
(8) (a) R. H. Eastman and L. K. Freeman, *J. Amer. Chem. Soc.*, 77, 6642 (1955); (b) L. I. Smith and E. R. Rogier, *ibid.*, 73, 3840 (1951); (c) R. J. Mohrbacker and N. H. Cromwell, *ibid.*, 79, 401 (1957); (d) A. L. Goodman and R. H. Eastman, *ibid.*, 86, 908 (1964); (e) C. H. Heathcock and S. R. Poulter, *ibid.*, 90, 3766 (1968).
(9) H. Bock and H. Alt, *ibid.*, 92, 1569 (1970), and previous references cited there.
(10) C. E. Coates, M. L. H. Green, and K. Wade, "Organometallic Compounds," Vol. II, Methuen, London, 1968, p 211, and references cited there.
(11) The structures of all new compounds were proved by nmr and ir spectra and by elemental analysis.
(12) The TCNE complex with VII is unstable. This frequency is calculated from the observed frequency of the VII–DCMA frequency using eq 19 and 20 of ref 3f.