

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  $^{18}\text{O}$  scrambling, intramolecularity of rearrangement in aromatic solvents,<sup>4</sup> and rate-determining deprotonation mechanism,<sup>13</sup> the present findings are compatible with a dual mechanism<sup>1,4,14</sup> 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-picoly radical, it then follows that the former should have smaller polarization. In view of the relative stability of acetoxy compared with methyl radicals,<sup>6</sup> 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

Received August 10, 1970

### $\sigma$ - $\pi$ Conjugation of Carbon-Metal Bonds. Stereoelectronic and Inductive Effects<sup>1,2</sup>

Sir:

A variety of chemical<sup>3a,4,5</sup> and spectroscopic<sup>3b,f,6</sup> 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,<sup>3b</sup> bent,<sup>3h</sup> stretched, or otherwise weakened  $\sigma$  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).

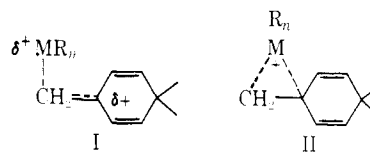
(5) Yu. G. Bundel, N.-D. Antonova, and A. O. Reutov, *ibid.*, **166**, 1103 (1966).

(6) (a) The ultraviolet spectra of A and B reported by Petrukov, Mironov, and Shorygin<sup>3b</sup> agree with this postulate. However, because uv transitions involve two orbitals, both having energies dependent upon

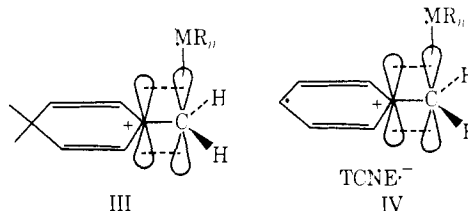


structural changes, these data have not been generally accepted as proof of  $\sigma$ - $\pi$  conjugation.<sup>7</sup> Thus allyl or benzyl metal compounds are usually

neighboring cationic centers by (vertical)<sup>3f,g</sup>  $\sigma$ - $\pi$  conjugation (I) rather than neighboring nucleophilic participation (II). It has been suggested<sup>3b,4</sup> that  $\sigma$ - $\pi$

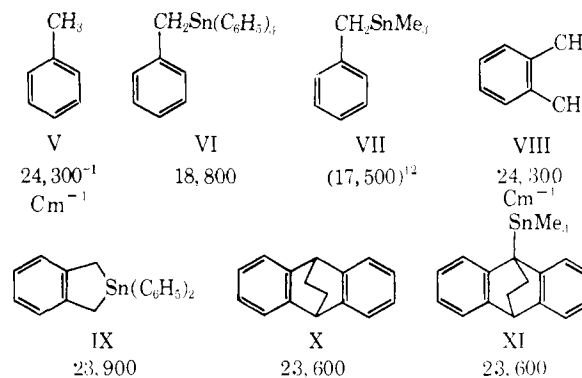


conjugation, like all other types of  $\pi$  conjugation, requires coplanarity of the C-M bond and the axis of the electron-deficient  $\pi$  orbital (or p orbital) as in III or IV.



We report here charge-transfer spectra which permit the separation of the large stereoelectronic effects of the C-MR<sub>n</sub>  $\sigma$  bond from the very small inductive effects of the -MR<sub>n</sub> group. The effects of changes in R upon the  $\sigma$ - $\pi$  conjugation of MR<sub>n</sub> are also reported.

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



In order to appreciate the enormous stabilization provided to cations by the -CH<sub>2</sub>Sn(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub> and -CH<sub>2</sub>-

discussed in terms of inductive effects<sup>9</sup> or d $\pi$ -p $\pi$  interactions<sup>10</sup> (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.<sup>8</sup>

(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.

$\text{SnMe}_3$  groups, we convert the observed frequencies to values of  $\sigma^+_{\text{CH}_3} = -0.25$ ,  $\sigma^+_{\text{CH}_2\text{Sn}(\text{C}_6\text{H}_5)_3} = -0.78$ ,  $\sigma^+_{\text{CH}_2\text{SnMe}_3} = -0.93$  by the method previously described.<sup>3f</sup> From these values we may see that the  $-\text{CH}_2\text{Sn}(\text{C}_6\text{H}_5)_3$  group is as activating as a methoxy group<sup>13a</sup> and the  $-\text{CH}_2\text{SnMe}_3$  group is almost as effective as an amino group. By substituting  $-\text{SnMe}_3$  for one of the  $\text{CH}_3$  hydrogens on toluene the rate of ring acetylation by Friedel-Crafts reaction<sup>13b</sup> would be accelerated by about  $10^6$ !<sup>14</sup>

But notice what happens when  $\text{Sn}(\text{C}_6\text{H}_5)_2$  is substituted for two  $\text{CH}_3$  hydrogens in going from VIII to IX. The charge-transfer frequency is slightly increased! A similar substitution of the more activating  $\text{SnMe}_3$  group for an  $\alpha$ -hydrogen in going from X to XI also results in negligible change. Clearly, when the C-metal bond is in the plane of the aromatic ring, the activation of that ring by the metal group completely disappears. Thus, a factor of  $>10^6$  in rate may be removed by rotating the C-metal bond away from the position of overlap with the  $\pi$  system.<sup>15</sup>

Having removed the  $\sigma$ - $\pi$  conjugation effect in structure XI we may now probe the inductive effect by replacing the  $-\text{SnMe}_3$  group in XI with other groups, e.g.,  $-\text{SiMe}_3$ ,  $-\text{HgC}_6\text{H}_{11}$ ,  $-\text{HgCl}$ . These substitutions have negligible effect on the CT frequencies indicating that *inductive effects of metallic groups,  $\text{MR}_3$ , in the  $-\text{CH}_2\text{MR}_n$  group are negligibly small.* It follows from the results with  $-\text{HgCl}$  and  $\text{HgC}_6\text{H}_{11}$  that the R groups also have *no direct field effect* in this group.

However, the groups R have a *very large indirect inductive effect* on the  $\text{CH}_2\text{MR}_n$  group. This is clearly seen in Figure 1 where the charge-transfer frequencies of benzyl-X and benzylmercuric-X are plotted<sup>16</sup> against  $\sigma_X^I$ . Equations for the two lines are

$$\nu_{\text{TCNE}}^{\text{PhCH}_2\text{X}} (\text{cm}^{-1}) = 4300\sigma_X^I + 24,250 \quad (1)$$

and

$$\nu_{\text{TCNE}}^{\text{PhCH}_2\text{HgX}} (\text{cm}^{-1}) = 11,200\sigma_X^I + 15,700 \quad (2)$$

Both the absolute values of the frequencies for a given X and the slopes<sup>13</sup> of the lines (sensitivity to X) indicate that the *indirect inductive effect* of X, operating through about 3.5 Å, is much greater than the direct-field effect of X operating through only 1.5 Å. This indirect effect can be interpreted as an inductive effect upon M which changes the ability of the  $-\text{MR}_n$  group to hyperconjugate.<sup>19</sup>

(13) (a) L. M. Stock and H. C. Brown, *Advan. Phys. Org. Chem.*, **1**, 89 (1963); (b) *ibid.*, **1**, 96 (1963).

(14) Even larger accelerations of ring electrophilic substitution reactions were observed with dibenzylmercury.<sup>3d</sup> Cleavage of C-metal bonds accompanies such ring substitutions.

(15) These results should be compared to similar studies on the (much smaller) effects of C-H hyperconjugation carried out by V. J. Shiner, Jr., *J. Amer. Chem. Soc.*, **82**, 2655 (1960).

(16) The charge-transfer frequencies of  $\text{TCNE}-\text{C}_6\text{H}_5\text{CH}_2\text{X}$  have been plotted against  $\sigma^*$  by H. Sakurai<sup>17</sup> who has proposed this as a measure of  $\sigma_X^*$ .

(17) H. Sakurai, private communication.

(18) D. N. Kravtsov and B. A. Faingor (*Izv. Akad. Nauk SSSR, Ser. Khim.*, **2**, 289 (1968)), studied the trinitrobenzene complexes with  $p\text{-Me}_2\text{NC}_6\text{H}_4\text{CH}_2\text{X}$  and  $p\text{-Me}_2\text{NC}_6\text{H}_4\text{CH}_2\text{HgX}$ . They observed that the effect of X in the mercury compound was somewhat less than its effect in  $p\text{-Me}_2\text{NC}_6\text{H}_4\text{CH}_2\text{X}$ . In this case, most of the charge in the cation radical is on nitrogen.

(19) The fact that  $-\text{CH}_2\text{CPh}_3$  or  $\text{CH}_2\text{CH}_2\text{OMe}$  is ineffective in  $\sigma$ - $\pi$  conjugation<sup>20</sup> argues against conjugative stabilization of  $\text{MR}_3$  of the type  $\text{R}_2\text{M}^{\delta+}=\text{R}^{\delta+}$ . The absence of delocalization of bonds to the positively charged metal is further indicated by the higher charge-transfer frequency of  $\text{PhCH}_2\text{SiPh}_3$  than of  $\text{PhCH}_2\text{SiMe}_3$ .<sup>20</sup>

(20) H. J. Berwin, unpublished results.

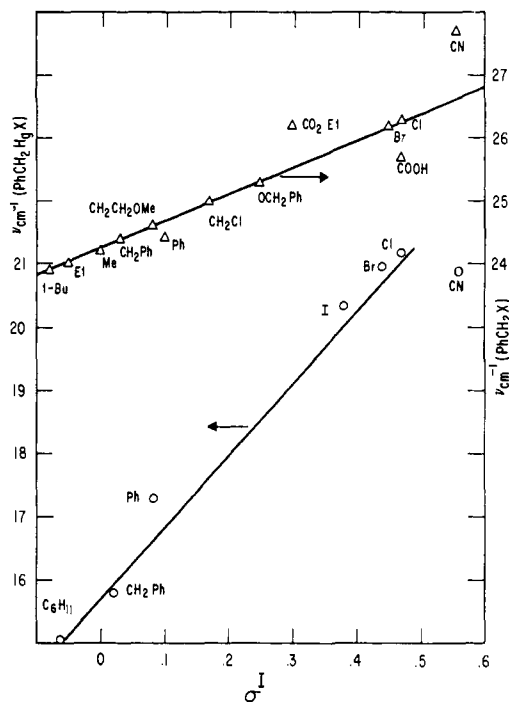
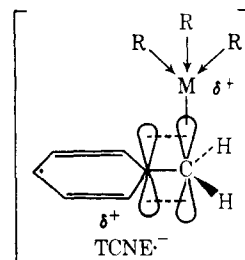


Figure 1. Plots of tetracyanoethylene charge-transfer frequencies of  $\text{PhCH}_2\text{X}$  ( $\Delta$ ) or  $\text{PhCH}_2\text{HgX}$  ( $\circ$ ) against  $\sigma^I$ . The left ordinate is for the lower plot and the right ordinate for the upper plot. Errors in frequency are about  $\pm 300 \text{ cm}^{-1}$ .

It thus appears that polarized  $\sigma$  bonds behave in every respect like  $n$  electrons on, e.g., nitrogen. The interesting point is that such  $\sigma$  bonds may be chosen



to have conjugating abilities over a range from no conjugation (e.g.,  $\text{MR}_n = \text{CF}_3$ ) to conjugation as effective as that of an amino group (e.g.,  $\text{MR}_n = -\text{HgC}_6\text{H}_{11}$ ).

\* Address correspondence to this author.

W. Hanstein, H. J. Berwin, T. G. Traylor\*

Chemistry Department, Revelle College  
University of California, San Diego  
La Jolla, California 92037

Received June 24, 1970

### Solvolysis of Bicyclo[3.2.1]octa-2,6-dienyl and Isomeric *p*-Nitrobenzoates<sup>1,2</sup>

Sir:

Bicyclooctadiene II has been reported by Brown and Ocolowitz<sup>3a</sup> to be more reactive than the monoene I in

(1) Research sponsored by the National Science Foundation.

(2) Reported in part at The Chemical Society 1967 Centenary lecture for the Symposium on "Some Aspects of Organic Reaction Mechanisms," London, England, Oct 10-20, 1967.

(3) (a) J. M. Brown and J. L. Ocolowitz, *Chem. Commun.*, 376 (1965); (b) J. M. Brown, *ibid.*, 639 (1967).