

also) which upon treatment with aqueous KCN releases 1,5-cyclooctadiene. Because of the generally low yields and long reaction time, use of iridium chloride presents no advantage over use of rhodium chloride for this isomerization.

CONTRIBUTION NO. 244
RESEARCH CENTER
UNITED STATES RUBBER COMPANY
WAYNE, NEW JERSEY

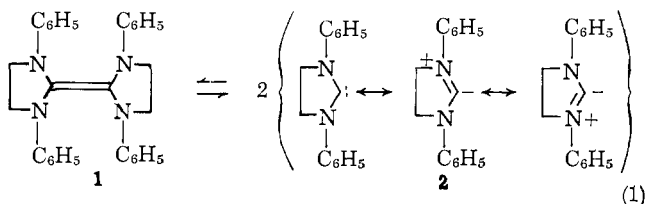
ROBERT E. RINEHART
JACK S. LASKY

RECEIVED APRIL 13, 1964

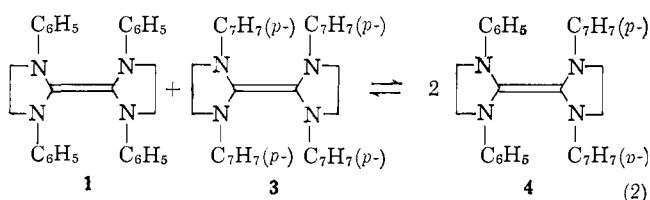
Tetraaminoethylenes. The Question of Dissociation

Sir:

Tetraaminoethylenes are distinguished both by the ardor and by the versatility of their chemical reactivity.^{1-3a} Wanzlick and his co-workers, whose researches are largely responsible for present knowledge of their chemistry, have proposed that the ethylenes dissociate readily and reversibly into divalent carbon derivatives, as illustrated for the best known tetraaminoethylene **1** in eq. 1. They have suggested that the reacting entity in virtually all of the transformations of **1** is the "nucleophilic carbene" **2**.¹ We wish to present evidence that the hypothetical dissociation equilibrium does not occur, even under rather vigorous conditions, and to propose an alternative mechanistic interpretation for reactions of tetraaminoethylenes.^{3b}



The question of dissociation was probed by a crossover experiment with a pair of tetraaminoethylenes. For the test to be fair, it was important that the two differ only subtly; hence the tetraphenyl derivative **1** and its *p*-tolyl analog **3**^{1d} were chosen. If dissociation were possible, it was expected that an equimolar mixture of **1** and **3** would give the crossed ethylene **4** in yields approaching the statistical 50% (eq. 2).



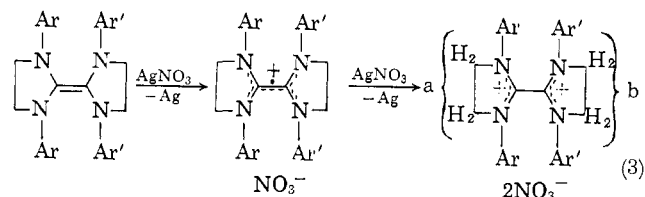
Ethylenes **1** and **3** crystallized in pure form when the corresponding 1,3-diarylimidazolium perchlorates were treated with the hindered base sodium tri-

(1) (a) H. W. Wanzlick, *et al.*, *Angew. Chem.*, **72**, 494 (1960); *ibid.*, **73**, 493, 764 (1961); (b) H. W. Wanzlick and E. Schikora, *Ber.*, **94**, 2389 (1961); (c) H. W. Wanzlick, *Angew. Chem. Intern. Ed. Engl.*, **1**, 75 (1962); (d) H. W. Wanzlick, F. Esser, and H. J. Kleiner, *Ber.*, **96**, 1208 (1963); (e) H. W. Wanzlick and H. J. Kleiner, *ibid.*, **96**, 3024 (1963).

(2) D. M. Lemal and K. I. Kawano, *J. Am. Chem. Soc.*, **84**, 1761 (1962).

(3) (a) R. L. Pruett, *et al.*, *ibid.*, **72**, 3646 (1950); N. Wiberg and J. W. Buchler, *Ber.*, **96**, 3223 (1963), and earlier papers. (b) Recent work by the latter authors has cast much doubt upon the existence of a dissociation equilibrium for tetrakis(dimethylamino)ethylene [*ibid.*, **96**, 3000 (1963)].

phenylmethoxide in dimethyl sulfoxide at 25°. Direct analysis of the products from the crossover experiment was out of the question because of the insolubility and the air-sensitivity of the ethylenes. Fortunately silver nitrate oxidized **1** and **3** via beautiful violet radical cations to the soluble, stable dinitrate salts **5**² and **6** (eq. 3). The reactions were rapid and the yields were 92 and 93%, respectively. Dinitrate **6** was obtained as orange needles from chloroform (m.p. 223-224° dec., *in vacuo*). *Anal.* Found: C, 65.12; H, 5.97; N, 13.20. The n.m.r. spectrum (D₂O) of **5** consisted of a complex multiplet centered at δ 7.7 p.p.m.⁴ corre-



- 1, Ar, Ar' = C₆H₅ 5, Ar, Ar' = C₆H₅
3, Ar, Ar' = C₇H₇(*p*-) 6, Ar, Ar' = C₇H₇(*p*-)
4, Ar = C₆H₅, Ar' = C₇H₇(*p*-) 7, Ar = C₆H₅, Ar' = C₇H₇(*p*-)

sponding to the aryl protons and a sharp singlet at δ 5.27 assignable to the methylene protons (relative areas, 5:2). Dinitrate **6** displayed an AB quartet (doublets centered at δ 7.67 and 7.35, *J* = 8.5 c.p.s.) for the ring protons and sharp singlets at δ 5.18 and 2.84 corresponding to the methylene and methyl protons, respectively (relative areas, 4:2:3).

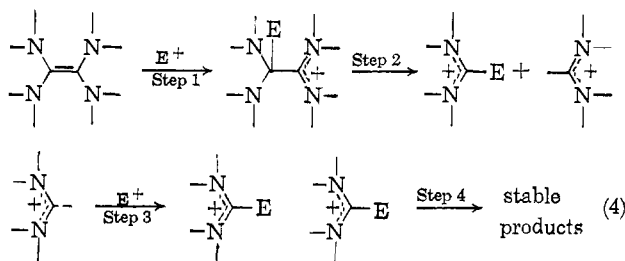
The upfield shift of 5 c.p.s. for the methylene protons of **6** relative to those of **5** suggested the possibility that the dinitrate **7** derived from the crossed ethylene **4** would be distinguishable by n.m.r. from **5** and **6**. A mixture containing **1**, **3**, and **4** was prepared as described above from equimolar amounts of 1,3-diphenylimidazolium and 1,3-di-*p*-tolylimidazolium perchlorates and oxidized to the dinitrate salts **5**, **6**, and **7**. The n.m.r. spectrum of the mixture in acetonitrile⁴ displayed a well-defined quartet in the methylene region (δ 4.78, 4.75, 4.72, and 4.69). Pure **5** and **6** gave rise to lines at δ 4.78 and 4.69, respectively, in acetonitrile, so the inner lines of equal intensity can be assigned to **7**. Peak areas indicated that cross product **7** comprised roughly half of the mixture, as expected on statistical grounds. We consider remarkable the 1.5-c.p.s. upfield shift of the signal for the a methylene protons of **7** compared with the corresponding line for **5**; similarly, the 1.5 c.p.s. downfield shift of the b proton signal relative to that for **6**. Clearly, the electron-donating influence of methyls in one "half" of the dication is readily discernible at the methylene protons in the other "half," despite the fact that ten bonds intervene.

A solution containing equimolar amounts of ethylenes **1** and **3** in carefully purified xylene was heated under reflux for 2 hr. in an atmosphere of oxygen-free nitrogen. The cooled reaction mixture was treated with silver nitrate in acetonitrile and the resulting dinitrates were collected by filtration and washed with ether (yield, 98%). In the methylene region of the n.m.r.

(4) All n.m.r. spectra were determined at 60 Mc./sec. Line positions for those measured in deuterium oxide are relative to external tetramethylsilane; those in acetonitrile were calibrated with the same reference internally. Acetonitrile was the solvent of choice for observing the methylene signals of the dinitrate salts since a small amount of HOD in the D₂O interfered somewhat.

spectrum of this mixture there appeared only a simple doublet corresponding to **5** and **6**; *no absorption attributable to the crossed ethylene 7 was present*. Hence the equilibrium represented by eq. 1 does not occur under conditions as drastic as *any* reported for reactions of tetraaminoethylenes.¹⁻³ A reconsideration of reaction pathways for tetraaminoethylenes is obviously necessary.

Every known reaction of the powerful π -bases can be interpreted in terms of electrophilic attack upon the π -electron system. Whereas the net effect of oxidizing agents such as silver ion and iodine is electron abstraction, leaving the skeleton intact,² most reactions of tetraaminoethylenes lead to products derived from only half of the molecule. It is proposed that the latter class of transformations (air oxidation excepted) conforms to a general mechanism expressed in simplest form by eq. 4, where E^+ represents an electrophile, charged or neutral. Analogy for steps 2 and 3 of eq. 4 is found in the work of Breslow,⁵ who has demonstrated that zwitterions of the type shown are effective both as leaving groups and as nucleophiles. The simplest example illustrating eq. 4 is the facile con-



version of a tetraaminoethylene into two moles of the related formamidinium salt with mineral acid ($E^+ = H^+$), but the proposal applies as well to reactions with hydroxylic substances, aldehydes, ketones, nitro compounds, negatively substituted olefins, etc.¹ In each of these kinds of compound either activated hydrogen or electron-deficient carbon is available as the electrophilic site.

Acknowledgment.—The authors wish to thank the National Science Foundation and the Research Committee of the University of Wisconsin for financial support. They are grateful also to Messrs. R. Lichter and C. Underbrink, who measured n.m.r. spectra.

(5) R. Breslow, *J. Am. Chem. Soc.*, **80**, 3719 (1958).

CHEMISTRY RESEARCH BUILDING
UNIVERSITY OF WISCONSIN
MADISON, WISCONSIN 53706

DAVID M. LEMAL
ROGER A. LOVALD
KENNETH I. KAWANO

RECEIVED MARCH 5, 1964

Electron Pairing and Linear H_3^+

Sir:

Shull¹ has recently criticized the view expressed by Hopton and Linnett² in a paper on linear H_3^+ . We showed that a wave function based on two "one-electron bonds" gave a lower energy than one based on the molecular orbital method or the valence bond method in the Coulson-Fischer form.³ More detailed calcula-

tions by Bowen and Linnett⁴ confirm the results obtained by Hopton and Linnett,² their calculations having been extended to H_3 and H_3^- .

Shull carries out an analysis in terms of natural orbitals. He shows that the MO pair description has a very large overlap with the best wave function (or alternatively that the first occupation number has a value very close to unity). He remarks correctly that the same is true for H_2 .⁵ However this does not alter the very serious fact that the MO pair description for linear H_3^+ leads to a poor energy for that ion, just as it does for H_2 . Moreover, for H_2 , this is true whatever form is allowed for the MO function.⁶ This is the weakness of the molecular orbital approach. It is also the weakness of all analyses in terms of natural orbitals which lay great stress on the large overlaps (or high first occupation numbers) but do not draw attention to the poor energy that is obtained using the first member alone despite its large occupation number. At no point in his paper¹ does Shull record a calculated energy, and in the first paragraph of his paper he states that the conclusions of Hopton and Linnett were based on the large overlaps. They were, in fact, based much more on the values obtained for the energy, the significant fact being that the deviation of the calculated energy from that obtained using the best equivalent CI function was about five times greater using the MO and VB functions than it was using the NP function.⁷ It is the chemist's misfortune that the energies that are of chemical importance are relatively small, being of a magnitude which are also produced by quite small changes in wave functions. Therefore the poor energies obtainable using an MO description (without CI) in nonempirical calculations of the present type are important to the chemist.

If the form of the "best CI function" is examined it can easily be seen that it suggests naturally the function Hopton and Linnett described as NP. Shull points out that this is the description that would be given by introducing electron correlation into a three-center bond description. This certainly provides another way of regarding the situation. Because we used, for our function, a semilocalized orbital involving one HH pair and another involving the other HH pair, and associated one electron with each, we described the distribution as consisting of two one-electron bonds. The spins of the electrons must be opposed (*i.e.*, the state must be a singlet) as otherwise the spin correlation effects would prevent the two electrons ever being simultaneously near the center of the system. Such an effect, driving the electrons onto the end atoms, would produce a considerable increase in energy. It is true therefore that the electron distribution, in this case, may equally well be described in terms of correlation within a three-center bond, or in terms of two one-electron bonds. The final choice between them must depend on which is more fruitful when there is need to transfer our ideas to other more complicated systems. It remains the opinion of the author that descriptions

(4) H. C. Bowen and J. W. Linnett, *Trans. Faraday Soc.*, submitted for publication.

(5) H. Shull, *J. Chem. Phys.*, **30**, 1405 (1959).

(6) C. A. Coulson, *Proc. Cambridge Phil. Soc.*, **34**, 204 (1938).

(7) In recent papers by Bowen and Linnett⁴ and by D. P. Chong and J. W. Linnett (*Mol. Phys.*, accepted for publication), it has been proposed that this method should be described as that of nonpaired spatial orbitals, NPSO.

(1) H. Shull, *J. Am. Chem. Soc.*, **86**, 1469 (1964).

(2) J. D. Hopton and J. W. Linnett, *J. Chem. Soc.*, 1553 (1962).

(3) C. A. Coulson and I. Fischer, *Phil. Mag.*, **40**, 386 (1949).