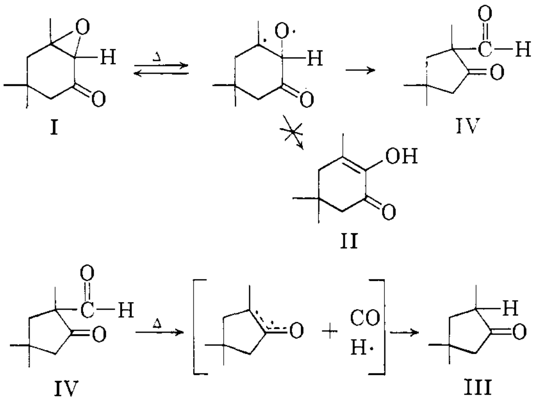
composition at 270° yielding the cyclopentanone III as the sole product.[11] A rationale for this thermal reaction is offered in Chart II. The absence of II in the products contrasts strikingly with its predominance in the radical process, and implies that the intermediate diradical produced by the reversible cleavage of the oxirane ring does not rearrange by a simple intramolecular hydrogen shift (Chart II). Instead, acyl group rearrangement again occurs, this time leading to the keto aldehyde IV. The subsequent thermal decarbonylation of IV easily was confirmed experimentally.[12] Furthermore radical initiating species are apparently produced in this process, since IV has proven to be a very efficient initiator for the radical chain reaction.

CHART II

THERMAL MECHANISM



The compounds encountered in this work have all been positively identified by physical and chemical comparisons with known substances.

It is of interest to note that the photochemical transformation of I does not lead to any of the products described in this report.[13]

[11] This thermal transformation is apparently a complex surface reaction, since a doubling of the surface area resulted in a 115% increase in the apparent first order rate constant. The last entry in the table describes another manifestation of this surface dependency.

[12] 2-Formyl-2,4,4-trimethylcyclopentanone (IV) was prepared by the method of H. O. House and R. L. Wasson, *J. Am. Chem. Soc.*, **79**, 1488 (1957), and exhibited a straightforward first order decomposition to III at 235°.

[13] Unpublished work of C. K. Johnson and W. Reusch.

[14] Portions of this work were reported at the 140th meeting of the American Chemical Society, Chicago, Illinois, September 7, 1961.

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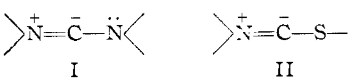
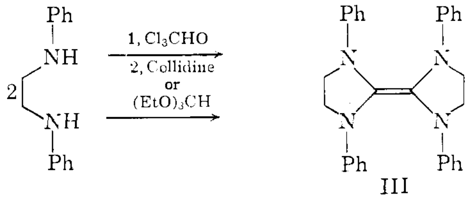
RECEIVED OCTOBER 4, 1961

STEPWISE ELECTRON ABSTRACTION FROM A TETRAAMINOETHYLENE

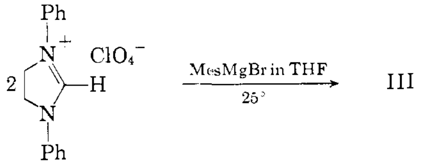
Sir:

Breslow's beautiful studies on the mechanism of thiamine action have demonstrated the remarkable facility with which zwitterions of the types I and II can be formed.[1] The presence of these species was revealed by their ability to undergo nucleophilic addition reactions as well as by deuterium exchange experiments. Recently Wanzlick[2] has succeeded in preparing the dimer (III) of a type I zwitterion by the two routes shown below.

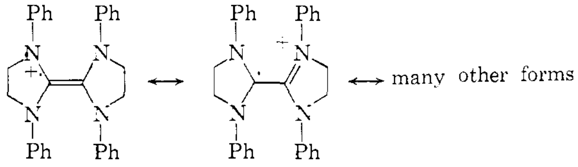




We wish to report a new synthesis for this substance and our findings on the nature of its ready oxidation. Whereas Wanzlick's routes to III required elevated temperatures, we have learned that 1,3-diphenylimidazolinium perchlorate is transformed into this compound by the action of the hindered base mesitylmagnesium bromide in tetrahydrofuran at room temperature.



The dimer III displays the intriguing property of forming violet solutions in a variety of solvents, a phenomenon attributed by Wanzlick to π-complex formation with the solvent Our observation that this color developed even in such solvents as dichloromethane cast considerable doubt on this hypothesis. When shaken with degassed acetonitrile, the dimer gave a colorless solution which rapidly became violet upon exposure to air, a fact which argued for oxidation of the ethylene to the radical cation IV reminiscent of a Wurster cation. Indeed, chloroform solutions of III in the air gave e.s.r. signals which varied in strength according to the intensity of the violet color.



IV

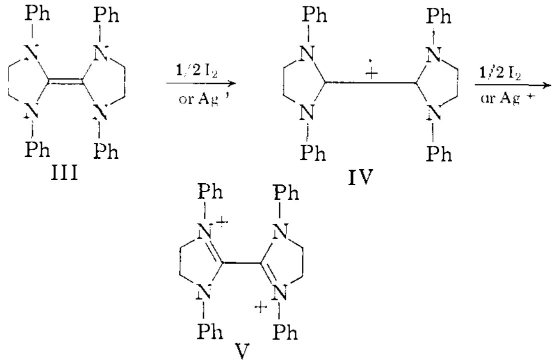
Solutions of IV prepared by air oxidation invariably faded a few minutes after air was excluded even when excess III was present. The further transformation of IV in air is not yet understood in detail, but it is known from Wanzlick's work[2] that the ultimate product of air oxidation of III is 1,3-diphenylimidazolid-2-one.

In contrast to the complex air oxidation, the action of iodine upon III proved to be clear-cut. Addition of an acetonitrile solution of iodine to a suspension of III in the same solvent led to the development of the intense violet color characteristic of IV, a color which did not disappear during two

[1] R. Breslow, *J. Am. Chem. Soc.*, **79**, 1762 (1957), and subsequent papers.

[2] H. W. Wanzlick, *et al.*, *Angew. Chem.*, **72**, 494 (1960); *ibid.*, **73**, 493 (1961); *Ber.*, **94**, 2389 (1961).

months in the absence of air. When III was treated with an entire mole of iodine, the initially formed radical cation disappeared and an orange-red solution remained. Concentration caused the solution to deposit orange-red crystals of the diiodide of V formed by transfer of a second electron to iodine. Purified by recrystallization from acetonitrile, the diiodide melted at 294–295°.



In a similar fashion, oxidation of III by silver nitrate in acetonitrile could be carried out in two discrete stages.[3] The violet color due to IV faded upon addition of a second equivalent of silver ion, leaving a yellow solution of the dinitrate. Canary yellow prisms of the dinitrate were obtained from acetonitrile/benzene (m.p. 242–243°). The corresponding diperchlorate was prepared from the ethylene III with silver perchlorate as the oxidizing agent (canary yellow crystals from acetonitrile, m.p. 341–342°).[4] *Anal.* Calcd. for $C_{30}H_{28}Cl_2N_4O_8$: C, 55.99; H, 4.38; N, 8.71. Found: C, 55.71; H, 4.63; N, 8.60. The disalts could be interconverted readily

$$\begin{tikzcd}\text{dinitrate} \arrow[r, "\text{KI}"] & \text{diiodide} \arrow[l, bend left, "\text{AgNO}_3"] \arrow[r, bend right, "\text{AgClO}_4"'] & \text{diperchlorate} \arrow[l, "\text{KI}"']\end{tikzcd}$$

Aqueous base rapidly cleaved the dinitrate into the two anticipated fragments, 1,3-diphenylimidazolid-2-one and N-formyl-N,N′-diphenylethylenediamine; they were isolated pure in 77 and 79% yield, respectively.

It is striking that the radical cation IV was formed when an acetonitrile suspension of III was treated with any one of the three disalts, thus demonstrating that electron abstraction from IV is freely reversible. Addition of excess iodide ion to a suspension of the diiodide failed to reverse the equilibria III $\rightleftarrows$ IV $\rightleftarrows$ V, but finely-divided silver proved to be a sufficiently powerful reducing agent in the presence of iodide ion to transform any of the disalts first to IV and then to III.

The e.s.r. spectrum of IV in chloroform is remarkable for its simplicity. From the analogy of IV to a Wurster cation, one would anticipate that the spin density of the unpaired electron would be large at the four nitrogen nuclei and quite likely measurable at the aromatic ring protons as well. Hyperfine splitting by the nitrogens alone would produce a nine line multiplet, but the observed spectrum consists of a single broad line (5.4 gauss at maximum slope) at $g = 2.0057 \pm 0.0001$. Although this suggests that the unpaired electron is localized on the central carbons, a simple LCAO-MO calculation for the tetraaminoethylene system strongly supports the idea that the delocalization energy of IV and the spin densities at nitrogen are large. That the absorption line shape for our dilute solutions is strictly Gaussian, not Lorentzian, appears to exclude the possibility that exchange interaction[5] is compressing the band width and obliterating fine structure.

Acknowledgment.—The authors wish to express their appreciation to Professors E. M. Kosower and R. West for helpful discussions, to Professor West and Mr. C. M. Lang for measuring the e.s.r. spectra, and to the National Science Foundation for financial assistance.

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[3] These iodine and silver ion oxidations parallel the experiments of D. H. Anderson, *et al.*, with tetrakis-(*p*-dimethylaminophenyl)-ethylene, *J. Am. Chem. Soc.*, **83**, 3157 (1961).

[4] All melting points are uncorrected. For the dinitrate, diperchlorate and diiodide salts it has been demonstrated that the melting points are strongly dependent upon the mode of recrystallization.

(5) D. J. E. Ingram, "Free Radicals as Studied by Electron Spin Resonance," Academic Press, Inc., New York, N. Y., 1958, Chap. 4; D. Kivelson, *J. Chem. Phys.*, **27**, 1087 (1957).

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RECEIVED MARCH 7, 1962

REACTIONS OF COÖRDINATED LIGANDS. II. NICKEL(II) COMPLEXES OF SOME NOVEL TETRADENTATE LIGANDS

Sir:

The area of "Reactions of Coördinated Ligands" is a new one and it is of that peculiar nature which should be of interest to chemists in a variety of fields. This communication provides a dramatic example of the role played by a metal ion in facilitating the formation of an organic molecule that is otherwise strongly discriminated against by competing reactions. In effect, the metal ion brings the reactants together in the product form that is most favorable for complexation.

The substances of immediate concern are the Schiff bases formed between α-diketones and β-mercaptoethylamine. Attempts to synthesize materials of this class by obvious routes yield thiazolines as major products, with some evidence for the formation of mercaptals and the desired α-diimines in low yields.

The structures of the diimines formed between α-diketones and β-mercaptoethylamine are sterically well suited to chelate in a tetradentate manner with square planar metal ions. In the design of these experiments, the coördination sphere of the metal ion is considered to serve as a slightly flexible template within which the coördination positions are in juxtaposition to the functional groups of the protracted ligand molecule. The chelate rings are expected to greatly stabilize the system for the complexing ability of the α-diimine linkage is well established[1,2] and recent work in these laboratories has led to the characterization of many planar

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(1) P. E. Figgins and D. H. Busch, *J. Am. Chem. Soc.*, **82**, 820 (1960).

(2) P. E. Figgins and D. H. Busch, *J. Phys. Chem.*, **65**, 2236 (1961).