The two-bond, carbon–phosphorus coupling in phosphines turns out to be positive, like the two-bond, carbon–fluorine coupling in *n*-hexyl fluoride. The two-bond, carbon–phosphorus coupling in phosphonium ions is negative, like the two-bond, carbon–proton coupling in ethane. The three-bond, carbon–phosphorus couplings are similar in magnitude and, as yet, of unknown sign. Phosphorus in phosphines, like fluorine, uses nearly pure p orbitals to form bonds to carbon.[13] In phosphonium ions it is reasonable to presume that hybrid orbitals are used. Negative one-bond couplings can occur when the energy difference between the valence s and p electrons becomes large, a situation implied by the formation of bonds involving unhybridized orbitals.[14]

Although the observed carbon–nitrogen couplings are internally consistent with the simplified formalism of the average-energy approximation,[15] a significant negative contribution to the couplings is apparent when these are compared with carbon–carbon couplings in similar situations.

More detailed discussion of these points along with comparisons of trends observed in nondirectly bonded and one-bond coupling constants will be presented later.

---

(13) From promotion energy arguments summarized by J. Hinze and H. H. Jaffé, *J. Am. Chem. Soc.*, **84**, 540 (1962).

(14) J. A. Pople and D. P. Santry, *Mol. Phys.*, **8**, 1 (1964).

(15) G. Binsch, J. B. Lambert, B. W. Roberts, and J. D. Roberts, *J. Am. Chem. Soc.*, **86**, 5564 (1964).

(16) National Science Foundation Predoctoral Fellow, 1965–1968.

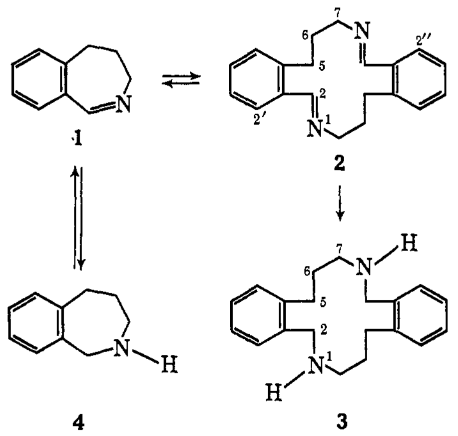
Frank J. Weigert,[16] John D. Roberts
Contribution No. 3858, Gates and Crellin Laboratories of Chemistry
California Institute of Technology, Pasadena, California 91109

Received May 12, 1969

A Novel Schiff Base Dimerization Reaction. Interconversions Involving the 3,4-Dihydro-5H-2-benzazepine and 3,4,10,11-Dibenzo-1,8-diazacyclotetradeca-1,3,8,10-tetraene Ring Systems

Sir:

We have observed that the crude monomeric product **1**, obtained by Bischler–Napieralski cyclization of N-formyl-3-phenylpropylamine with polyphosphoric acid–phosphorus pentoxide at 160° for 16 hr, is transformed on standing for 16 hr to a crystalline dimer, 3,4,10,11-dibenzo-1,8-*trans,trans*-1,8-diazacyclotetradeca-1,3,8,10-tetraene (**2**): mp 172–173°; ir ($CHCl_3$) 6.11, 6.24, and 6.36 (w) μ; nmr ($CDCl_3$, TMS) δ 8.46 (2, broad s, $H_{2,9}$), 7.87 (2, m, $H_{2',2''}$), 7.28 (6, m), 3.37 (4, m, NCH_2), 2.93 (4, t, $J = 6.5$ Hz), and 2.18 ppm (4, m); mass spectrum, *m/e* 290 (m^+). Assignment of the *trans,trans*-di-Schiff base structure rests on (a) the azomethine proton absorption at 8.46 ppm, (b) the observed deshielding[1] ($\Delta = -0.59$ ppm) of $H_{2'}$ and $H_{2''}$, and (c) sodium borohydride reduction to the diamine **3**: mp 164–164.5°; nmr ($CDCl_3$, TMS) δ 7.18 (8, s), 3.70 (4, s, $H_{2,9}$), 2.90 (4, t, $J = 7.5$ Hz, $H_{5,12}$), 2.75 (4, m, $H_{7,14}$), 1.95 (4, m), and 2.07 ppm (2, broad s, NH); mass spectrum, *m/e* 294 (m^+).



Insight into the dimerization mechanism[2] was derived from the observation that the *reverse reaction*, conversion of dimer **2** to monomer **1**, occurred readily when ir and nmr samples of **2** were left standing in chloroform solution for several hours. In a controlled experiment dimer **2** was unchanged during 1 hr in solution in purified $CDCl_3$ (nmr); addition of 0.1 mole of trifluoroacetic acid led, in 70 min, to essentially complete conversion to **1**: nmr ($CDCl_3$, TMS) δ 8.49 (1, broad s), 7.27 (4, m), 3.62 (2, t, $J = 6$ Hz, NCH_2), 2.76 (2, *t*, $J = 6.5$ Hz), and 2.22 ppm (2, m); ir ($CDCl_3$) 6.10 (m), 6.17, 6.26 (vw), and 6.36 μ; mass spectrum, *m/e* 145 (m^+); picrate mp 159–160°. Evaporation of the $CDCl_3$ *in vacuo* afforded oil **1** which dimerized rapidly: within 1 min the oil became viscous; within 3 min dimer **2** began to crystallize out. Rapid treatment of the oil **1** with an excess of methanolic sodium borohydride afforded the amine **4**: mass spectrum, *m/e* 147 (m^+); hydrochloride mp 220–222° (lit.[3] mp 223–225°).

The instability of both dimer **2** in solution and monomer **1** neat, in the presence of acid, is in marked contrast to the behavior of **2** and **1** in the absence of acid. A pure sample of **1**, obtained by oxidation of **4** in refluxing benzene for 10 min with azeotropically activated manganese dioxide,[4] remained liquid for more than 1 hr. Upon standing overnight, however, about 50% conversion to dimer **2** resulted. Dimer **2** is thermally stable, small samples subliming at 145° (0.03 mm) or distilling at 185° (0.03 mm) without change.

It can be concluded on the basis of the present data that, while other pathways may be available, the facile interconversions involving **1** and **2** in this work are acid catalyzed. The observation of essentially complete monomerization of **2** in acidic chloroform solution, and dimerization of **1** neat, suggest comparable stabilities for monomer and dimer. Studies to determine the equilibrium constant for this reaction are in progress.

A simple stepwise scheme, involving a 1,3-diazetidine intermediate, can be envisioned for the acid-catalyzed interconversions of **1** and **2**. Schiff base dimerizations

---

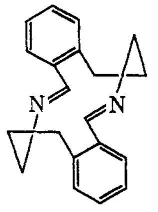
(1) *Cf.* lower field proton resonances for comparably disposed *ortho* protons in the *trans* rings for a variety of imines: D. Y. Curtin, E. J. Grubbs, and C. G. McCarty, *J. Am. Chem. Soc.*, **88**, 2775 (1966).

(2) The dimerization could result from an uncatalyzed, acid-catalyzed, or water-catalyzed process. For example, the hydrolysis of **1** by a catalytic amount of water to an open-chain amino aldehyde followed by dehydrative dimerization could yield **2**. M. E. Derieg, R. M. Schweininger and R. I. Fryer, *J. Org. Chem.*, **34**, 179 (1969), have observed the formation of a 3,4,11,12-dibenzo-1,5,9,13-tetraazacyclohexadeca-1,3,9,-11-tetraene-6,14-dione from a 3,4-dihydro-1,5-benzodiazocine-2-one precursor.

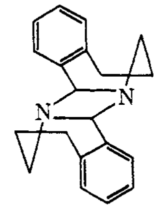
(3) N. S. Hjelte and T. Agback, *Acta Chem. Scand.*, **18**, 191 (1964).

(4) I. M. Goldman, *J. Org. Chem.*, **34**, 1979 (1969).

to 1,3-diazetidines and Schiff base exchange reactions *via* diazetidines have been reported.[5] We saw no evidence for diazetidine intermediates in the present work. Examination of Dreiding and/or Corey–Pauling–Koltun models of all the various geometrical and conformational possibilities for both dimer **2** and the assumed diazetidine intermediate suggests that the most stable configurations for **2** and the intermediate are the *trans*,-*trans* "chair" structure **5** and the *cis,anti,cis* structure **6**, respectively.[6] In **5** the imine dipoles are already closely aligned for facile bond formation to give **6**. The models of **5** also show that the diamagnetic shift of the N–CH_2 protons in **2** relative to **1** (Δ = +0.25 ppm) can be ascribed to the phenyl ring current effect in the unstrained conformations of **2**. The deshielding of the benzylic protons in **2** relative to **1** (Δ = −0.17 ppm) may be the result of the close proximity of these protons in **2** to the deshielding cones of the imine groups. The models of **5** and **6** show that introduction of methyl groups into the 2 and 9 positions of **5**, and into the corresponding positions of the diazetidine ring of **6**, would result in severe overcrowding, especially in **5**. This would result in the destabilization of dimer relative to monomer, thereby accounting for the observation that the 1-methyl analog of **1** showed no tendency to dimerize.



5



6

Identical dimerization–monomerization reactions also occur in the Bischler–Napieralski sequence with N-formyl-3,4-dimethoxyphenylpropylamine. In this regard we have repeated a portion of the work of Kanaoka, *et al.*,[7] and found that their structures "IVa" and "Va" are actually dimers corresponding to **2** and **3**.[8] We are presently investigating other examples of imine dimerizations as a route to medium-ring di-Schiff bases.

---

[5] C. K. Ingold and H. A. Piggott, *J. Chem. Soc.*, 121, 2793 (1922); 123, 2745 (1923).

[6] Structures 5 and 6 appear to have the least strain and the fewest nonbonded interactions of the various possibilities. The tricyclic system in 6 has the four-membered ring fused in the most stable (*cis*, pseudo-equatorial) conformation to the seven-membered rings.

[7] Y. Kanaoka, E. Sato, O. Yonemitsu, and Y. Ban, *Tetrahedron Letters*, 2419 (1964).

[8] This conclusion is based on careful comparison of our data with the reported[7] data. Our melting points were higher than those reported. In our hands, the polyphosphoric ester procedure led to products showing appreciable and varying amounts of ether interchange; pure products were obtained using polyphosphoric acid and/or phosphorus pentoxide.

Irving M. Goldman, Jerry K. Larson
James R. Tretter, Edmund G. Andrews
Medical Research Laboratories
Chas. Pfizer & Co., Inc., Groton, Connecticut 06340

Received June 4, 1969

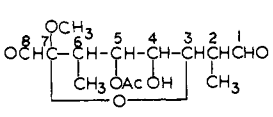
Additions and Corrections

Organic Sulfur Chemistry. I. The Disulfide–Phosphine Reaction. Desulfurization with Tris(diethylamino)phosphine [*J. Am. Chem. Soc.* **90,** 4181 (1968)]. By DAVID N. HARPP, JOHN G. GLEASON, and JAMES P. SNYDER, Department of Chemistry, McGill University, Montreal, Quebec, Canada.

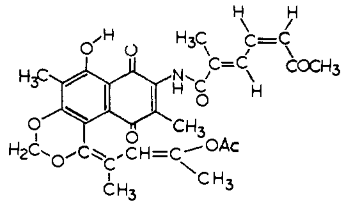
The fifth disulfide in Table I should appear as C_6H_5-SCH_3.

Chemistry of the Streptovaricins. V. Structures of Streptovaricins A and C [*J. Am. Chem. Soc.*, **90,** 6241 (1968)]. By KENNETH L. RINEHART, JR., HARI H. MATHUR, KAZUYA SASAKI, PRESTON K. MARTIN, and CHARLES E. COVERDALE, Department of Chemistry and Chemical Engineering, University of Illinois, Urbana, Illinois 61801.

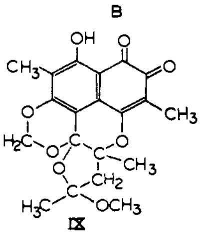
Structures I, II, and IX were omitted from the published manuscript.



I



II



IX

Triplet–Triplet Energy Transfer from the Second Triplet States of Anthracenes. Chemical Studies [*J. Am. Chem. Soc.*, **91** 1492 (1969)]. By ROBERT S. H. LIU and JAMES