

(CO)<sub>6</sub> slowly and with decomposition dissolved in perchloric acid; attempts to isolate salts were unsuccessful.

Structure I assigned to these salts is supported by the increased carbonyl frequencies in the spectra. Similar shifts generally are caused by a positive charge in the metal carbonyl moiety. It is most straightforward to assume that the seven olefinic carbon atoms are lying in one plane, whereas the CH<sub>2</sub>-group in the molecule is pointed upward or downward. The n.m.r. spectrum of the C<sub>8</sub>H<sub>9</sub>Fe(CO)<sub>3</sub><sup>+</sup> cation in sulfuric acid shows four absorptions, at -168, -17, +162 and +225 c.p.s. (relative to water), with intensity ratios of 1:4:2:2. This result can be rationalized readily in terms of the proposed structure.

In general, the unoccupied orbitals of all stable conjugated cyclic hydrocarbons are antibonding. Protonation will produce an unoccupied non-bonding orbital which when formed in a transition metal complex may be used for electron back-donation. In accord with theoretical conclusions by Brown<sup>7</sup> the presence of low lying orbitals will stabilize metal-ligand bonding, especially of the last members of the first transition metal series. Recently a number of similar salts of the cyclohexadienium- and cycloheptadienium- iron tricarbonyl cation have been described.<sup>8,9,10</sup> The cyclooctatrienium-iron-tricarbonyl-cation is thus a higher member of a class of transition metal complexes with resonance stabilized carbonium ions.

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- (7) Ref. 5; *J. Inorg. Nucl. Chem.*, **10**, 49 (1959); **13**, 212 (1960).  
 (8) E. O. Fischer and R. D. Fischer, *Angew. Chem.*, **72**, 919 (1960).  
 (9) H. J. Dauben and D. J. Bertelli, *J. Am. Chem. Soc.*, **83**, 497 (1961).  
 (10) G. Winkhaus and G. Wilkinson, *Proc. Chem. Soc.*, 312 (1960).

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#### A PHOTOCHEMICALLY-INDUCED, VALENCE-BOND TAUTOMERISM IN A SIX-MEMBERED AROMATIC SYSTEM

Sir:

Photochemically-induced valence-bond tautomerisms, or "bond-switching" reactions, have received considerable recent attention, particularly in cyclic trienones,<sup>1-6</sup> cyclic dienones<sup>7-9</sup> and cyclic dienes<sup>10,11</sup> and trienes.<sup>11</sup> Analogous reactions in six-membered aromatic systems, which would lead to products corresponding to the "Dewar" structure for benzene, have not been observed. It seemed

- (1) F. Santavy, *Biol. Listy*, **31**, 246 (1950).  
 (2) R. Grewe and W. Wolf, *Ber.*, **84**, 621 (1951).  
 (3) E. J. Forbes, *J. Chem. Soc.*, 3864 (1955).  
 (4) O. L. Chapman and D. J. Pasto, *J. Am. Chem. Soc.*, **80**, 6685 (1958).  
 (5) O. L. Chapman and D. J. Pasto, *ibid.*, **82**, 3642 (1960).  
 (6) W. G. Dauben, K. Koch, O. L. Chapman and S. L. Smith, *ibid.*, **83**, 1768 (1961).  
 (7) D. H. R. Barton, *Helv. Chim. Acta*, **42**, 2604 (1959).  
 (8) G. Buchi and E. M. Burgess, *J. Am. Chem. Soc.*, **82**, 4333 (1960).  
 (9) J. J. Hurst and G. H. Whitham, *Proc. Chem. Soc.*, 116 (1961).  
 (10) O. L. Chapman and D. J. Pasto, *Chem. and Ind.*, 53 (1961).  
 (11) W. G. Dauben and R. L. Cargill, *Tetrahedron*, **12**, 186 (1961).

to us that such a high-energy system might be formed by irradiation of an acid salt of a 2-aminopyridine, since the formation of a cyclic amidine salt might give partial diene character to the remaining aromatic bonds. We wish to report in this Communication the successful realization of this prediction with the isolation and characterization of a valence-bond tautomer of 2-amino-5-chloropyridine (I).

Irradiation of I (*pK<sub>a</sub>* 4.7 in water: HCl salt, m.p. 192–194°, λ<sub>max</sub><sup>H<sub>2</sub>O</sup> 238, 315 mμ; ε, 6780, 2770) in dilute hydrochloric acid with sunlight through Pyrex glass resulted in the gradual separation of colorless crystals (*pK<sub>a</sub>* 8.4 in water, m.p. 205.5–207° with rapid heating, m.p. 202.5–204° with moderate heating, m.p. 192–194° with very slow heating, indicating complete reconversion to I·HCl before melting) which were characterized both as a monohydrate (*Anal.* Calcd. for C<sub>5</sub>H<sub>5</sub>N<sub>2</sub>Cl·H<sub>2</sub>O·HCl: C, 32.9; H, 4.4; N, 15.3; Cl (total), 38.8. Found: C, 32.9; H, 4.4; N, 15.6; Cl (total), 38.1) and as a hemihydrate (*Anal.* Calcd. for C<sub>5</sub>H<sub>5</sub>N<sub>2</sub>Cl·1/2H<sub>2</sub>O·HCl: C, 34.5; H, 4.1; N, 16.1; Cl (ionic), 20.4. Found: C, 34.0; H, 4.5; N, 16.1; Cl (ionic), 18.7) depending upon drying conditions. An aqueous solution of this material was transparent to ultraviolet light above 260 mμ, with only end absorption below 260 mμ (ε, 3230 at 220 mμ). The spectrum of I was gradually restored when this solution was allowed to stand at room temperature. Rate constants for the reconversion (in spectroscopic concentrations) of the photoisomer to I were 6 × 10<sup>-4</sup> min.<sup>-1</sup> (27 ± 2°) in water and 140 × 10<sup>-4</sup> min.<sup>-1</sup> (27 ± 2°) in 0.1 N sodium carbonate. In non-spectroscopic concentrations, reconversion of the photoisomer to I upon neutralization was essentially instantaneous and quantitative.

The n.m.r. spectrum (identical for the monohydrate and the hemihydrate) in D<sub>2</sub>O of the photoisomer shows an equal intensity doublet in the vinyl hydrogen region (τ = 3.45, 3.59, coupling constant, 8 cps).<sup>12</sup> These values compare favorably with those recently reported by Dauben and co-workers<sup>6,11</sup> for the vinyl hydrogens in certain cyclobutene derivatives. Furthermore, each component of the original doublet could be further resolved into a sharp doublet with a coupling constant of approximately 2 cps. The spectrum also shows peaks consistent with the presence of bridgehead hydrogens in a cyclobutane ring adjacent to an electron-withdrawing group (τ = 5.9, 5.4, 5.2, with other peaks possibly obscured by a strong water peak). These values are comparable to those found for the cyclobutyl hydrogens in the dimer of N-methyl-2-pyridone (τ = 5.6 and 5.8).<sup>13</sup>

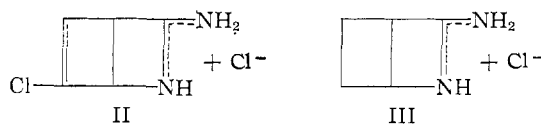
Catalytic reduction of the photoisomer with hydrogen and platinum oxide in aqueous solution yielded a product (m.p. 333–335° dec.; *Anal.* Calcd. for C<sub>5</sub>H<sub>8</sub>N<sub>2</sub>·HCl: C, 45.3; H, 6.85; N, 21.1; Cl, 26.75. Found: C, 45.1; H, 6.7; N, 20.7; Cl, 26.3) which was transparent to ultra-

(12) All n.m.r. spectra were determined on both 40 and 60 megacycle Varian instruments.

(13) E. C. Taylor and W. W. Paudler, *Tetrahedron Letters*, **25**, 1 (1960), and unpublished results.

violet light above 240  $m\mu$ , with only end absorption below 240  $m\mu$  ( $\epsilon$ , 5600 at 220  $m\mu$ ). The n.m.r. spectrum of this reduction product shows a broad hydrogen peak ( $\tau = 7.89$ ) and a pair of doublets ( $\tau = 5.79, 5.66$  and  $5.29, 5.15$ ), typical of an AB pattern. Integration showed that there are twice as many hydrogen atoms under the broad peak as in the combined doublets. Although the reduction product (as the hydrochloride), in contrast to the photoisomer, was stable upon prolonged standing in aqueous solution, addition of 0.1 *N* sodium hydroxide at room temperature resulted in the separation within two minutes and in essentially quantitative yield of a compound which, on the basis of all available evidence, appears to be *cis*-2-aminocyclobutanecarboxamide IV, (m.p. 253–255°; *Anal.* Calcd. for  $C_5H_{10}N_2O$ : C, 52.6; H, 8.8; N, 24.5; mol. wt., 114. Found: C, 52.95; H, 9.0; N, 24.9; mol. wt. (in glacial HOAc), 99).

On the basis of the above considerations, we feel that the photoisomer of I can only be represented by structure II, and that the reduction product must be represented by structure III. The conversion of I to II represents the first example of a valence-bond tautomerism in a six-membered aromatic system. The reaction appears to be general, for similar photoisomers were obtained from 2-aminopyridine and 2-amino-5-bromopyridine; catalytic reduction in each case yielded compound III. Furthermore, the conversion of II to IV in an over-all yield of greater than 95% promises to be representative of an extraordinarily simple route to cyclobutane derivatives. Extensions of this new photoisomerization reaction to other systems and the chemistry of the photo products are under active exploration.



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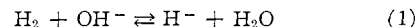
#### BASE CATALYZED HOMOGENEOUS HYDROGENATION

Sir:

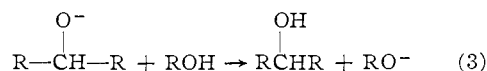
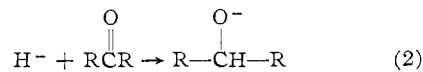
Although the reaction of molecular hydrogen with unsaturated organic molecules at moderate temperatures is generally energetically feasible, a potential barrier to the process exists which is only overcome by the use of heterogeneous catalysts or certain transition-metal complexes in homogeneous systems.<sup>1</sup>

Two groups of observations of long standing in the literature suggested to us that simple basic catalysis of homogeneous hydrogenation also

might be achieved in suitable systems. The first of these is the base catalyzed exchange between  $D_2$  and water,<sup>2</sup> which is pictured most easily in terms of the (admittedly very unfavorable) equilibrium



Conceivably, the small amount of hydride ion present in strongly basic systems might accomplish the reduction of an organic molecule via a sequence such as



Second, a considerable number of reactions are known in which the treatment of organic molecules with strong bases at elevated temperatures leads to oxidation with evolution of molecular hydrogen. Perhaps the oldest is the Varrentrapp reaction in which caustic fusion of oleic acid produces hydrogen, palmitic acid and acetic acid.<sup>3</sup> Since at least one step in these processes involves dehydrogenation, they may be considered as simply the back reactions of a based catalyzed hydrogenations.

TABLE I

BASE CATALYZED HYDROGENATIONS IN *tert*-BUTYL ALCOHOL

Substrate	<i>T</i> (°C.)	$H_2$ (lb./in. <sup>2</sup> )	Time, hr.	$KOC_4H_9^a$	Yield, <sup>b</sup> %
Benzophenone	200	1300	70	0.5	50–60
Benzophenone	180	2000	16	0	—
Benzophenone	195	1900	31	0.25	40–50
Benzophenone	230	2560	15	0	—
Benzophenone	230	2560	15	0.2	+ <sup>d</sup>
Benzophenone	170	2100	25	0.05	(–) <sup>c</sup>
Nitrobenzene	160	1900	45	0.1	+
Nitrobenzene	160	2000	49	0	—

<sup>a</sup> Moles/mole substrate. <sup>b</sup> (+) indicates reduction, but yield not determined; (–) indicates no reaction. <sup>c</sup> Small pressure drop, but no reduction products definitely identified. <sup>d</sup> Teflon liner in vessel.

We now report such a base-catalyzed homogeneous hydrogenation, achieved by heating benzophenone in *tert*-butyl alcohol solution containing potassium *tert*-butoxide at 200° under 1300–2000 lb./in.<sup>2</sup> hydrogen pressure. Hydrogen is slowly absorbed and benzhydrol obtained in 40–60% yield, determined by gas chromatography, and identified by retention time, infrared spectra, and mixed melting point. No further reduction to diphenylmethane is detected.

Experiments were carried out in a small conventional stirred autoclave with nickel liner, and the effects of variables are shown in Table I. Hydrogen, *tert*-butoxide and an elevated temperature are all required for the reaction. The possibility of heterogeneous catalysis by the nickel liner is eliminated by the successful experiment using a Teflon liner.

(2) K. Wirtz and K. F. Bonhoeffer, *Z. physik Chem.*, **177A**, 1 (1936); W. K. Wilmarth, J. C. Dayton and J. M. Flournoy, *J. Am. Chem. Soc.*, **75**, 4549 (1953); S. L. Müller and D. Rittenberg, *ibid.*, **80**, 64 (1958).

(3) F. Varrentrapp, *Liebigs Ann.*, **35**, 196 (1840). For more recent work, cf. R. G. Ackman, P. Linstead, B. J. Wakefield and B. C. L. Linstead, *Tetrahedron*, **8**, 221 (1960).

(1) For a review and discussion, cf. J. Halpern, *Advances in Catalysis*, **9**, 302 (1957).