

tion and esterification with diazomethane, a 45% yield of the β -keto ester V ($R = \text{CH}_3$, $R' = \text{CO}_2\text{-CH}_3$) 2,4-dinitrophenylhydrazone m.p. 184–185.5° (Found: C, 56.15; H, 5.96). (The β -keto ester, V, $R = \text{CH}_3$, $R' = \text{CO}_2\text{Et}$, also could be obtained by the use of ethyl chlorocarbonate in benzene, but the yield was lower.) The substance showed the expected⁶ absence of enolic properties (infrared, ferric chloride), but alkylation of the salt (NaH) with methyl iodide, then hydrolysis and decarboxylation, gave the known 1,4a-dimethyl-2-decalone (V, R, $R' = \text{CH}_3$) identified by mixed melting point of its 2,4-dinitrophenylhydrazone m.p. 185–186° (reported⁷ m.p. 186°) with that of an authentic sample.

The success of the trapping of the enolate ion IV depends on the alkylation reaction being faster than equilibration of the initially produced enolate IV to the more stable II *via* proton transfer with some initially formed neutral alkylated ketone. In the same manner transfer of proton between the monoalkylated ketone and unchanged anion will lead to di-(and poly)alkylation. The success of the alkylation in liquid ammonia solution suggests that *in that solvent* the alkylation is faster than the enolate equilibration. However, exchange of the ammonia for *dimethyl sulfoxide* before alkylation of IV, $R = \text{H}$, with butyl iodide led to a monobutyldecalone which was shown to be the 3-butyl compound III ($R = \text{H}$, $R' = \text{Bu}$) by comparison with an authentic sample made by an unambiguous route (2,4-dinitrophenylhydrazone, m.p. 173–174.5° (Found: C, 61.97; H, 7.32)).

When, on the other hand, treatment of the enolate ion IV, $R = \text{CH}_3$, with butyl iodide was carried out *in liquid ammonia* the monobutyl compound, formed in 50% yield, turned out to be again the product of trapping without rearrangement, the 1-butyl derivative V ($R = \text{H}$, $R' = \text{Bu}$), identical with an independently synthesized authentic sample (2,4-dinitrophenylhydrazone, m.p. 125–126.5°) (Found: C, 62.16; H, 7.34).

It is evident from these results that proton transfer reactions which lead to equilibration of the anions are, perhaps not unexpectedly, much more affected by the extent of dissociation of the enolate ion-lithium cation ion pair than is the C-alkylation reaction⁸ and that the sequence described here may—if it can be extended—be a solution to the problem of directing alkylation to a specific α -carbon of an unsymmetrical ketone.

(6) Cf. F. Sondheimer, R. Mechoulam and M. Sprecher, *Tetrahedron Letters*, No. 22, 38 (1960).

(7) M. Yanagita and R. Futaki, *J. Org. Chem.*, **21**, 949 (1956).

(8) Cf. D. Cram, B. Rickborn and G. R. Knox, *J. Am. Chem. Soc.*, **82**, 6412 (1960).

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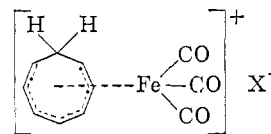
SALTS OF THE CYCLOOCTATRIENIUM IRON TRICARBONYL CATION

Sir:

Since the discovery of cyclooctatetraene iron carbonyl complexes by at least three independent

research groups in 1958 to 1959,^{1,2,3} these compounds have received much attention. The mononuclear $\text{C}_8\text{H}_8\text{Fe}(\text{CO})_3$ is particularly interesting as the results of nuclear magnetic resonance measurements indicate that all four double bonds of the C_8H_8 ring are involved in the bonding to iron. It has been proposed by several authors^{1,4,5} that in this complex the C_8H_8 should be planar. However, the results of a recent refined spectroscopic investigation make it increasingly apparent that at least deviations from perfect planarity must be present⁶; the question is not yet fully settled. The complex is remarkably stable. It dissolves in, and is recovered from, anhydrous acetic acid without decomposition. Also, it fails to decolorize bromine, and resists hydrogenation and normal Diels-Alder reactions.

It now has been observed by the writer that $\text{C}_8\text{H}_8\text{Fe}(\text{CO})_3$ is converted into a salt of composition $\text{C}_8\text{H}_9\text{Fe}(\text{CO})_3^+\text{BF}_4^-$ if it is dissolved in an ethereal solution of fluoroboric acid. This compound forms yellow crystals (m.p. gradual darkening above 150°). *Anal.* Calcd.: Fe, 16.8; C, 39.8; H, 2.7. Found: Fe, 16.7; C, 39.4; H, 2.9; infrared (Nujol), carbonyl region, 4.70 μ (neat), 4.84 μ (broader). It readily dissolves in water, acetone and methanol, is almost insoluble in ether and in non-polar solvents. Aqueous solutions are stable at room temperature but undergo hydrolysis when heated: $\text{C}_8\text{H}_8\text{Fe}(\text{CO})_3$ can be recovered from such solutions by extraction with benzene. If to



Structure I

the solutions of $\text{C}_8\text{H}_9\text{Fe}(\text{CO})_3^+\text{BF}_4^-$ sodium tetraphenylborate or Reinecke salt is added, salts of the complex cation with the corresponding anions are formed. Similarly, $\text{C}_8\text{H}_8\text{Fe}(\text{CO})_3$ dissolves in 70–80% HClO_4 . Upon addition of water, yellow crystals of the perchlorate, $\text{C}_8\text{H}_9\text{Fe}(\text{CO})_3^+\text{ClO}_4^-$, precipitate. This was found to be violently explosive in the dry state; C–H analysis was not possible. *Anal.* Calcd.: Fe, 16.2. Found: Fe, 16.2; infrared (Nujol), carbonyl region, 4.69 (neat), 4.81 μ (broader). Finally, $\text{C}_8\text{H}_8\text{Fe}(\text{CO})_3$ was found to dissolve even in concentrated hydrochloric acid. The yellow needles of the hydrochloride (m.p. 61° dec.) separate upon cooling the solution of $\text{C}_8\text{H}_8\text{Fe}(\text{CO})_3$ in ethereal hydrogen chloride. *Anal.* Calcd.: Fe, 19.9; C, 47.1; H, 3.2; Cl, 12.6. Found: Fe, 19.5; C, 47.8; H, 3.44; Cl, 11.1; infrared (Nujol), carbonyl region, 4.72, 4.84 and 4.89 μ respectively. The hydrochloride slowly decomposes at room temperature. The binuclear complex $\text{C}_8\text{H}_8\text{Fe}_2$

(1) T. A. Manuel and F. G. A. Stone, *Proc. Chem. Soc.*, 90 (1959); *J. Am. Chem. Soc.*, **82**, 366 (1960).

(2) M. D. Rausch and G. N. Schrauzer, *Chemistry and Industry*, 957 (1959).

(3) A. Nakamura and N. Hagihara, *Bull. chem. Soc. (Japan)*, **32**, 880 (1959).

(4) F. A. Cotton, *J. Chem. Soc.*, 400 (1960).

(5) D. A. Brown, *J. Inorg. Nucl. Chem.*, **10**, 39 (1959).

(6) Personal communication from Dr. H. P. Fritz, Munich.

(CO)₆ 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 CH₂-group in the molecule is pointed upward or downward. The n.m.r. spectrum of the C₅H₉Fe(CO)₃⁺ 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 Brown⁷ 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.^{8,9,10} The cyclooctatrienium-iron-tricarbonyl-cation is thus a higher member of a class of transition metal complexes with resonance stabilized carbonium ions.

Acknowledgment.—I wish to thank Miss U. Merkel for her skillful experimental assistance.

- (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,¹⁻⁶ cyclic dienones⁷⁻⁹ and cyclic dienes^{10,11} and trienes.¹¹ 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_a* 4.7 in water: HCl salt, m.p. 192-194°, λ_{max}^{H₂O} 238, 315 mμ; ε, 6780, 2770) in dilute hydrochloric acid with sunlight through Pyrex glass resulted in the gradual separation of colorless crystals (*pK_a* 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 C₅H₅N₂Cl·H₂O·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 C₅H₅N₂Cl·1/2H₂O·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 × 10⁻⁴ min.⁻¹ (27 ± 2°) in water and 140 × 10⁻⁴ min.⁻¹ (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 D₂O of the photoisomer shows an equal intensity doublet in the vinyl hydrogen region (τ = 3.45, 3.59, coupling constant, 8 cps).¹² These values compare favorably with those recently reported by Dauben and co-workers^{6,11} 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).¹³

Catalytic reduction of the photoisomer with hydrogen and platinum oxide in aqueous solution yielded a product (m.p. 333-335° dec.; *Anal.* Calcd. for C₅H₈N₂·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.