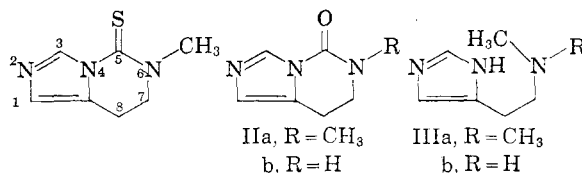


rare for a thiourea derivative to occur in Nature.⁴

Zapotidine, m.p. 96–98°, $C_7H_9N_3S$,² contains one N-methyl group (Found: N-methyl, 8.88), no S-methyl, O-methyl or C-methyl groups and no active hydrogen functions. On attempted microhydrogenation (platinum, acetic acid), no hydrogen was absorbed after one hour. The n.m.r. spectrum⁵ showed two aromatic proton peaks (at 505 cps. due to the C-3 proton and at 408 cps. due to the C-1 proton), an N-methyl proton peak (at 213 cps.) and two aliphatic proton peaks (triplets centered at 220 cps. due to the C-7 protons and at 183 cps. due to the C-8 protons).

Zapotidine on being boiled with ethanolic silver nitrate solution, with gradual addition of aqueous sodium hydroxide,⁶ yielded the urea derivative IIa, m.p. 115–116°, $C_7H_9N_3O$ (Found: C, 55.71;



H, 6.11; N, 27.12; S, 0.00); $\lambda_{\text{max}}^{\text{EtOH}}$ 222 m μ (ϵ 8,100); $\nu_{\text{max}}^{\text{KBr}}$ 1713 cm.⁻¹. The ultraviolet and infrared data are compatible with those reported for the corresponding des-methyl compound IIb.³ The n.m.r. spectrum⁵ showed peaks at 485 cps. (C-3 proton), 405 cps. (C-1 proton), a triplet at 209 cps. (C-7 protons), 188 cps. N-methyl protons) and a triplet at 182 cps. (C-8 protons). Integration of the n.m.r. peaks showed a total of nine protons to be present.

Lithium aluminum hydride reduction of zapotidine^{3,7} gave N α ,N α -dimethylhistamine (IIIa), characterized as the dipicrate, m.p. 231–233°, $C_{19}H_{19}N_5O_4$ (Found: C, 38.39; H, 3.31; N, 21.07). The latter derivative was identified (mixture m.p., infrared comparison) with an authentic sample (m.p. 231–233°).⁸

Boiling zapotidine in ethanol with 20% aqueous potassium hydroxide yielded N α -methylhistamine (IIIb), converted to the dipicrate, m.p. 188–190°, $C_{18}H_{17}N_5O_4$ (Found: C, 37.21; H, 3.04; N, 21.66; O, 37.50). This derivative was identified (mixture m.p., infrared comparison) with an authentic sample (m.p. 187–189°).⁹

The above-described findings unequivocally show zapotidine to possess structure I. Two other compounds isolated from *Casimiroa edulis*, N α ,N α -

dimethylhistamine (IIIa)^{8b,10} and casimiroedine,^{9b} are imidazoles structurally closely related to I and a biogenetic relationship between the three substances appears very probable. Moreover, it is tempting to speculate that biogenetically zapotidine is derived from 1-acetyl-(or thioacetyl)-histamine by ring closure and methylation. 1-Acetyl-imidazoles have been postulated to be of importance as part of the active sites of some enzymes.¹¹

We are indebted to Dr. S. Pinchas (Weizmann Institute of Science) for valuable discussions regarding infrared spectra, to Prof. R. T. Major (University of Virginia) for providing a sample of N α ,N α -dimethylhistamine dipicrate and to Prof. C. Djerassi (Stanford University) for a sample of N α -methylhistamine dipicrate.

(10) J. S. L. Ling, S. Y. Pan and F. A. Hochstein, *J. Pharmacol. Exptl. Therap.*, **122**, 44A (1958).

(11) For a review see E. A. Barnard and W. D. Stein in "Advances in Enzymology," ed. F. F. Nord, **20**, 51 (1958); but see also M. A. Marini and G. P. Hess, *J. Am. Chem. Soc.*, **82**, 5160 (1960).

DANIEL SIEFF RESEARCH INSTITUTE
WEIZMANN INSTITUTE OF SCIENCE
REHOVOTH, ISRAEL
RESEARCH LABORATORY, VARIAN A.G.
ZÜRICH, SWITZERLAND
SYNTEX, S. A., APART. POST. 2679
MEXICO D.F., MEXICO

R. MECOULAM
F. SONDHEIMER
A. MELERA
F. A. KINCL

RECEIVED MARCH 6, 1961

CHEMISTRY OF VANADIUM HEXACARBONYL, I: π -CYCLOHEPTATRIENYL-TRICARBONYL- VANADIUM(-1)

Sir:

Various complexes containing a transition metal bonded to a seven-membered carbocyclic system have been synthesized in the recent past, e.g., $C_7H_5Cr(CO)_3$,¹ $C_7H_5Mo(CO)_3$,¹ $C_7H_5W(CO)_3$,² and $C_7H_5Fe(CO)_3$.³ The first tropylium sandwich compound to be described was the ionic $[C_7H_7-Mo(CO)_3]BF_4$; subsequently the neutral $C_7H_7VC_5H_5$ ⁴ was reported.

We now wish to report the synthesis of a novel organometallic vanadium compound and present evidence which supports the assignment of its structure as tropylium-tricarbonyl-vanadium(-1).

Vanadiumhexacarbonyl was prepared from its diglyme-complexed sodium salt as described elsewhere.⁶ The agitated mixture of 8.7 g. (0.04 mole) of $V(CO)_6$ and 18.4 g. (0.2 mole) of cycloheptatriene in 300 ml. of *n*-hexane was heated to its reflux temperature of about 65° for one hour, under nitrogen. During this time 2.7 liters of gas (S.T.P., 0.12 mole) were evolved, containing only a mere trace of hydrogen. Some fine brown amor-

(4) See M. G. Ettlinger and J. E. Hodgkins, *J. Org. Chem.*, **21**, 204 (1956).

(5) N.m.r. spectra were determined at 60 Mc. on a Varian V 4300-C spectrometer in deuteriochloroform solution with tetramethylsilane as internal standard.

(6) See A. E. Dixon, *J. Chem. Soc.*, **67**, 556 (1895); A. Kjaer and R. Gmelin, *Acta Chim. Scand.*, **10**, 1100 (1956).

(7) See V. M. Micovic and M. L. Mihailovic, *J. Org. Chem.*, **18**, 1190 (1953).

(8) (a) C. F. Huebner, R. A. Turner and C. R. Scholz, *J. Am. Chem. Soc.*, **71**, 3942 (1949); (b) R. T. Major and F. Dürsch, *J. Org. Chem.*, **23**, 1564 (1958).

(9) (a) B. Garforth and F. L. Pyman, *J. Chem. Soc.*, 489 (1935); (b) C. Djerassi, C. Bankiewicz, A. L. Kapoor and B. Riniker, *Tetrahedron*, **2**, 168a (1958).

(1) E. W. Abel, M. A. Bennett, R. Burton and G. Wilkinson, *J. Chem. Soc.*, 4559 (1958).

(2) T. A. Manuel and F. G. A. Stone, *Chemistry & Industry*, 231 (1960).

(3) H. J. Dauben, Jr., and D. J. Bertelli, *J. Am. Chem. Soc.*, **83**, 497 (1961).

(4) H. J. Dauben, Jr., and L. R. Honnen, *ibid.*, **80**, 5570 (1958).

(5) R. B. King and F. G. A. Stone, *ibid.*, **81**, 5263 (1959); **82**, 4557 (1960).

(6) R. P. M. Werner and H. E. Podall, *Chemistry & Industry*, 144 (1961).

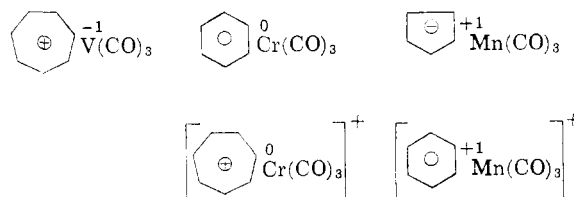
phous solid had formed. The warm mixture was filtered, painstakingly excluding air and using filter-aid. The volume of the clear green *n*-hexane solution was reduced in vacuum to about 30 ml. The concentrated solution afforded shiny dark crystals upon cooling to Dry Ice temperature. The yield was 1.9 g. (21%) after two recrystallizations from *n*-hexane. The compound sublimed readily at 60° (0.1 mm.); it melted, in a sealed capillary under nitrogen, at 134–137°, with decomposition. It was stable in air for several hours, insoluble in water and readily soluble in most organic solvents such as methanol, diethyl ether, diglyme, acetone, chloroform, carbon tetrachloride and petroleum ether to give air-sensitive green solutions. *Anal.* Calcd. for $C_{10}H_7O_3V$: C, 53.12; H, 3.12; V, 22.54; mol. wt., 226.11. Found: C, 53.0; H, 3.44; V, 22.5; mol. wt., 220 (Signer method, in CH_2Cl_2).

Although these analytical results are in accord with the given composition, the alternative possibility of a cycloheptatriene-tricarbonyl-vanadium, $C_7H_5V(CO)_3$, could not be ruled out solely on this basis. Conclusive evidence for the proposed structure was furnished by the magnetic properties of the compound, whose diamagnetism is compatible only with a monomeric $C_7H_5V(CO)_3$.⁷ The infrared spectrum of the compound exhibited two sharp CO stretching bands at 1915 and 1975 cm^{-1} in *n*-heptane solution; when taken from a KBr wafer, these absorptions were slightly shifted to 1875 and 1950 cm^{-1} , respectively. Other absorptions of the KBr disk were at 785, 1430 and 3375 cm^{-1} .

The given structure assignment seems to be compatible with the n.m.r. spectrum of the compound which, in $CDCl_3$ using tetramethylsilane as an internal reference, shows only a symmetrical doublet centered at 312 cps. (the individual peaks of about equal intensity being at 305 and 318 cps.).⁸ The absence of the cycloheptatriene system is thus clearly indicated, although the reasons for this splitting are not fully understood at present.⁹

Tropylium-tricarbonyl-vanadium(−1) is a compound of considerable theoretical interest, being isoelectronic with the neutral complexes benzene-tricarbonylchromium(0)¹⁰ and cyclopentadienyl-tricarbonylmanganese(+1)¹¹ as well as with the diamagnetic cations [tropylium-tricarbonyl-

chromium(0)]⁺¹² and [benzene-tricarbonyl-manganese(+1)]⁺¹³



Comparison of the three neutral complexes, which contain the iso- π -electronic systems $C_7H_7^+$, C_6H_6 and $C_5H_5^-$, respectively, shows a distinct increase in stability with the decreasing electronegativity of the complexed metals, their formal oxidation states being V(−1), Cr(0) and Mn(+1), respectively. This is well in agreement with theoretical considerations; the maximum stability, oxidatively and thermally, in this series of transition metal complexes is naturally to be expected in that case where the metal does retain a positive charge increment.¹⁴

Noteworthy, the reaction of $[Na \text{ diglyme}_2]^- [V(CO)_6]$ with tropylium bromide, in aqueous solution as well as in isoöctane, did not furnish the described tropylium compound but yielded vanadium carbonyl and ditropyl. A similar oxidation-reduction process had been observed previously when $Na[C_5H_5Cr(CO)_3]$ was treated with tropylium bromide.^{1,15}

(12) J. D. Munro and P. L. Pauson, *Proc. Chem. Soc.*, 267 (1959).

(13) T. H. Coffield, V. Sandel and R. D. Closson, *J. Am. Chem. Soc.*, **79**, 5826 (1957).

(14) See also P. L. Pauson, *Proc. Chem. Soc.*, 301 (1960).

(15) E. O. Fischer and H. P. Fritz, "Advances in Inorganic Chemistry and Radiochemistry," Vol. 1, pp. 107–109, Academic Press, New York, N. Y., 1959.

RESEARCH LABORATORIES
ETHYL CORPORATION
DETROIT, MICH.

ROBERT P. M. WERNER
SWITLANA A. MANASTYRSKYJ

RECEIVED FEBRUARY 15, 1961

THE MECHANISM OF THE NITRAMINE REARRANGEMENT

Sir:

The acid-catalyzed rearrangement of aromatic nitramines to *o*- and *p*-nitroanilines¹ as an example of the mechanistically enigmatic, purportedly intramolecular aromatic rearrangements. Therefore, the mechanism of this process is of some theoretical interest. In order to define the course of this reaction we have intensively investigated the isomerization of *N*-nitro-*N*-methylaniline and its derivatives. The mechanism shown is consistent with our findings.

Isotope dilution analysis of the product from reaction of *N*-nitro-*N*-methylaniline-*C*-14 in 0.1 *N* hydrochloric acid at 40° indicated that 52.1% *o*-nitro-*N*-methylaniline, 30.9% *p*-nitro-*N*-methylaniline, 9.9% *N*-methylaniline, and no *m*-nitro-*N*-methylaniline were formed. This analysis was

(7) We are indebted to Professor S. Kirschner at Wayne State University, Detroit, Michigan, for carrying out the magnetic susceptibility measurement.

(8) We are indebted to Mr. LeRoy F. Johnson of Varian Associates, Palo Alto, Calif., for this measurement, taken on a 60 mc. high resolution spectrometer.

(9) Following a suggestion kindly made by one of the referees, the n.m.r. spectrum was also recorded at 40 mc., in $CHCl_3$ and CS_2 solutions, using a spectrometer made available to us by the General Motors Technical Center, Warren, Mich. These spectra, however, showed only one wide and unresolved absorption at about 215 c.p.s. from tetramethylsilane, thus supplement the statement concerning absence of the C_7H_5 system. Since support of this statement was the principal objective of the n.m.r. spectroscopic measurements, a more complete evaluation of these data is presently considered beyond the scope of this communication.

(10) E. O. Fischer and K. Öfele, *Chem. Ber.*, **90**, 2532 (1957); B. Nicholls and M. C. Whiting, *J. Chem. Soc.*, 551 (1959). G. Natta, R. Ercoli and F. Calderazzo, *Chim. e ind. (Italy)*, **40**, 287 (1958).

(11) E. O. Fischer and R. Jira, *Z. Naturforsch.*, **9b**, 618 (1954).

(1) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp. 625–629.