The reactions were studied in molar proportions such that there existed initially a 1:1 ratio of Ca to Sn atoms. The amounts of reactants and the volume of water used in each case were adjusted such that the initial concentration of tin(II) was in the range 0.03–0.05 M for each reaction studied. A solid phase persisted throughout the duration of each reaction. Initially this solid was simply calcium hydroxylapatite, then a mixture of partially reacted materials, and finally the completed reaction products. The reactions were carried out at reflux temperature in an inert atmosphere of nitrogen gas from which all traces of oxygen had been removed by bubbling the gas through a train of wash bottles containing amalgamated zinc and solutions of vanadium(II) ions.[5] This precaution also was employed during filtration of the reaction mixtures in order to prevent any air oxidation of the tin(II) ion.

All products were dried either *in vacuo* over P_4O_{10} or by use of a conventional drying pistol. Identifications were made by means of X-ray diffraction powder patterns when possible, along with chemical analyses. A modification of the Martin–Doty method[6] was used for the colorimetric determination of phosphate; tin(II) was determined by an accurate procedure which we devised in this laboratory and which soon will be published elsewhere.

Results and Discussion.—A summary of the reactions studied is given in Table I.

TABLE I

PRODUCTS OBTAINED BY AQUEOUS TREATMENT OF $Ca_{10}(PO_4)_6(OH)_2$ WITH TIN(II) SALTS

Tin(II) salt used	Reaction time, hr.	Final pH of soln.	Insoluble products
SnF_2	48	3.00	$Ca_{10}(PO_4)_6(OH)_2$, $Sn_4(PO_4)_2$-$(OH)_2 \cdot H_2O$, CaF_2
SnF_2	72	2.85	$Ca_{10}(PO_4)_6(OH)_2$, $Sn_4(PO_4)_2$-$(OH)_2 \cdot H_2O$, CaF_2
SnF_2	96	2.75	$Sn_4(PO_4)_2(OH)_2 \cdot H_2O$, CaF_2
$SnSO_4$	48	2.40	$Sn_4(PO_4)_2(OH)_2 \cdot H_2O$, $CaSO_4 \cdot 2H_2O$
$SnClF$	48	2.65	$Sn_4(PO_4)_2(OH)_2 \cdot H_2O$, CaF_2
Sn_2ClF_3	60	2.80	$Sn_4(PO_4)_2(OH)_2 \cdot H_2O$, CaF_2
$SnCl_2 \cdot 2H_2O$	48	2.50	$Sn_3(PO_4)_2$

The pH of these solutions was affected both by the hydrolysis of the tin(II) ion as represented by the equation $Sn^{+2} + H_2O \rightarrow SnOH^+ + H^+$, and by the relative basicities of the individual anions. The 1:1 ratio of Sn:Ca was employed on the basis of the assumption that a simple cationic exchange would take place and lead to the formation of tin-(II) hydroxylapatite, $Sn_{10}(PO_4)_6(OH)_2$. However, the absence of a tin(II) phosphate with molar Sn/PO$_4$ ratio of 1.67 among any of the products eliminated this possibility.

In order to identify the basic tin(II) phosphate, which was formed in all but one of the reactions studied, a sample of it had to be separated from the accompanying insoluble by-products present in each of the mixtures obtained. This was necessary because X-ray diffraction studies of

these various mixtures revealed that the pattern of the basic tin(II) phosphate did not agree with any published for known phosphate compounds of tin(II) and hence it could not be identified simply by comparison. All attempts at isolating this material from mixtures containing the very insoluble CaF_2 were unsuccessful. In strong acid solutions CaF_2 exhibits sufficient solubility to permit its removal, but such conditions also cause a change in the structure of the basic tin(II) salt. Attempted extractions of the calcium with chelating agents such as EDTA were also inefficient under the mildly acidic conditions required to prevent alteration of the structure of $Sn_4(PO_4)_2(OH)_2 \cdot H_2O$. However, isolation of this compound was effected by treating the mixture containing $CaSO_4 \cdot 2H_2O$ with a buffer solution of pH 4; gypsum is readily soluble under these conditions even at room temperature and the basic tin(II) phosphate remains unchanged.

Later, in succeeding studies, $Sn_4(PO_4)_2(OH)_2 \cdot H_2O$ also was obtained directly as a hydrolysis product of $SnHPO_4$. The complete results of our investigations regarding the hydrolysis of $SnHPO_4$ will be discussed in a later publication.

The assignment of the empirical formula $Sn_4(PO_4)_2(OH)_2 \cdot H_2O$ to this basic salt was based on its composition as determined by chemical analyses. The same procedure was used for the identification of $Sn_3(PO_4)_2$ as the product obtained from the reaction between $Ca_{10}(PO_4)_6(OH)_2$ and $SnCl_2 \cdot 2H_2O$. The X-ray diffraction pattern of our tribasic tin(II) phosphate did not agree with that published for this compound in the ASTM X-ray card file.

Finally, we have found that SnF_2, $Sn_2P_2O_7$, and $Ca_{10}(PO_4)_6(OH)_2$ in the molar ratio of 10:1:1, respectively, react to form $Sn_3(PO_4)_2$ and CaF_2.

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THE REDUCTION OF OLEFINS BY MEANS OF AZODICARBOXYLIC ACID in situ

Sir:

Certain considerations[1] led us to the belief that the readily available[2] salts of azodicarboxylic acid might be a source of H_2N_2 (diimide, diazene), which, although at present a poorly defined species,[3] should act *in situ* as a potent reducing agent. We have now found that the aforementioned salts do

(5) L. Meites and T. Meites, *Anal. Chem.*, **20**, 984 (1948).

(6) J. B. Martin and D. M. Doty, *ibid.*, **21**, 965 (1949).

(1) Chemical reductions of olefins by means of hydrazine (*e.g.*, F. Aylward and M. Sawistowska, *Chem. and Ind.*, 404 (1961), and previous papers) has been shown to be oxygen dependent (*ibid.*, 433 (1961) and by independent observation in this Laboratory). Also, in the acidification of potassium azodicarboxylate (J. Thiele. *Ann.*, **271**, 127 (1892)) nitrogen and hydrazine are formed in addition to carbon dioxide. For this decomposition Thiele suggested diimide as an intermediate which would disproportionate into nitrogen and hydrazine. In the hydrazine reductions it was considered possible that the reaction with olefins was preceded by air oxidation to diimide, the active reducing agent and the possible intermediate in the azodicarboxylic acid decomposition.

(2) Prepared by hydrolysis of azodicarboxamide (Thiele, ref. 1), commercially available from Aldrich Chemical Company, Milwaukee, Wisconsin.

(3) (a) L. F. Audrieth and B. A. Ogg, "The Chemistry of Hydrazine," John Wiley and Sons, Inc., New York, N. Y., 1951, Chapter 6; (b) S. N. Foner and R. L. Hudson, *J. Chem. Phys.*, **28**, 719 (1958); (c) D. A. Dows, G. C. Pimentel and E. Whittle, *ibid.*, **23**, 1606 (1955).

in fact effect under appropriate conditions saturation of several, randomly chosen model olefins.

In general the reductions were carried out by stirring a solution of the unsaturated compound in an organic solvent with an azodicarboxylate salt and added carboxylic acid (two equivalents with respect to the azodicarboxylate to effect its decomposition) under nitrogen for three to twelve hours at room temperature. Reductions which were carried out in methanol with sodium azodicarboxylate (100% excess) and acetic acid gave the following results: elaidic acid to stearic acid (62% by infrared analysis and titration with iodine monobromide); oleic acid to stearic acid (51% by infrared spectra and titration), and quinine to dihydroquinine (78% by quantitative hydrogenation). Reduction of allyl alcohol in β-ethoxyethanol with potassium azodicarboxylate (20% excess) and octanoic acid catalyst gave 1-propanol (78% by gas chromatography and infrared spectra of the products, and similarly cyclohexene gave cyclohexane (10% by gas chromatography. Finally, a reduction of azobenzene in methanol with potassium azodicarboxylate (20% excess) and acetic acid catalyst gave a quantitative yield of hydrazobenzene, m.p. 125–126°, mixed m.p. 125–126.5° (less than 1% azobenzene by ultraviolet spectroscopy).

Although several mechanistic interpretations for these reductions present themselves, diimide is implicated. The utility of this substance as a reagent in the field of organic chemistry has not been recognized heretofore, but the potential for liberation of elemental nitrogen suggests that its reducing power should be substantial. Through the agency of azodicarboxylic acid salts, the reactivity with other types of materials is currently under investigation in this Laboratory.

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1-METHYL-π-ALLYLIRONTRICARBONYL CHLORIDE

Sir:

During the course of an earlier investigation, butadiene irontricarbonyl was found to react with anhydrous hydrogen chloride in room temperature to yield compound I as the only isolable organometallic. Yields ranged from 30 to 45%. Compound I was obtained as a yellow-brown solid, m.p. 58–60°, which decomposed rapidly at temperatures above the melting point, although it was relatively stable at room temperature. Purification could be effected by low temperature recrystallization from hydrocarbon solvents, or sublimation at room temperature and 0.05 mm. pressure. Elemental analysis showed I to be a 1:1 adduct of butadiene irontricarbonyl and hydrogen chloride. Magnetic susceptibility measurements showed the complex to be diamagnetic.[1] It was insoluble in,

(1) We wish to thank Professor S. Kirschner of Wayne State University, Detroit, Michigan, for these measurements.

and unaffected by, water and soluble in a broad variety of organic solvents.

Anal. Calcd. for $C_7H_7O_3ClFe$: C, 36.5; H, 3.14; Cl, 15.4; Fe, 24.3. Found: C, 36.8; H, 3.28; Cl, 15.6; Fe, 24.3.

The spectral characteristics of I are in complete accord with the proposed π-allyl structure, being basically the same as those exhibited by the cobalt[2] and manganese[3] compounds, II and III, respectively.
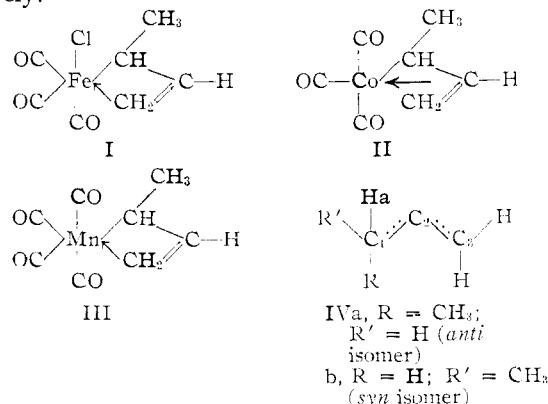
The infrared spectrum of I has four metal carbonyl bands at 2041, 2000, 1961, and 1923 cm.$^{-1}$. The band at 1520 cm.$^{-1}$ was assigned to the π-allyl C=C vibration. Absorptions are also present at 1385 cm.$^{-1}$ for the methyl group, and at 3086 and 3012 cm.$^{-1}$ for the =CH stretch.

The nuclear magnetic resonance spectrum of I in carbon tetrachloride (60 mc.) possesses four general bands whose integrated intensities are in the ratio of 1:2:1:3. The group of lines centered at 5.08 τ represents Ha[4] (see structures IV). The pair of doublets centered at 5.83 and 7.10 τ represent the *syn* and *anti* hydrogens on C₃. Furthermore, the relative intensity of the doublet centered at 5.83 τ, plus an unsymmetrical broadening of the base on the high field side, indicate a masking of the lines predicted for the hydrogen on C_1. The doublet centered at 7.93 τ is from the methyl group hydrogens.

Among other products, a mixture of butenes is formed on thermal decomposition of I. This precise behavior is exhibited by the above mentioned cobalt compounds.[5] When a solution of I in benzene is refluxed, ferrous chloride is precipitated and carbon monoxide is evolved smoothly until 50% of the theoretical amount has been given off. Gas evolution stops abruptly at this point. Butenes were evolved and trapped out. They were identified by mass spectrometry, vapor phase chromatography, and comparison of the bromination products with authentic samples. The reaction mixture was shown by vapor phase chromatography to contain only butadiene irontricarbonyl. The products formed suggest that the decomposi-

(2) H. B. Jonassen, R. I. Stearns, J. Kenttämaa, D. W. Moore and A. G. Whittaker, *J. Am. Chem. Soc.*, **80**, 2586 (1958).

(3) W. R. McClellan, H. H. Hoehn, H. N. Cripps, E. L. Muetterties and R. W. Howk, *ibid.*, **83**, 1601 (1961).

(4) The nomenclature used in this paper is that proposed by McClellan, *et al.*, in reference 3.

(5) C. L. Aldridge, H. B. Jonassen, and E. Pulkkinen, *Chem. and Ind.* 374 (1960).