

TABLE I

Compound	Absorptions ^a (cm. ⁻¹) Lithium Fluoride Optics				
	w is weak, m is medium, s is strong				
Mn ₂ (CO) ₁₀		2044 m	2012 s	1981 m	
Tc ₂ (CO) ₁₀		2064 m	2016 s	1981 m	
Re ₂ (CO) ₁₀		2070 m	2012 s	1974 m	
Mn(CO) ₅ I	2125 w	2044 s		2003 m	
Tc(CO) ₅ I	2146 w	2055 s		2000 m	
Re(CO) ₅ I	2145 w	2042 s		1987 m	
(Mn(CO) ₄ I) ₂		2087 w	2033 s	2009 m	1976 m
(Tc(CO) ₄ I) ₂		2108 w	2042 s	2012 m	1975 m
(Re(CO) ₄ I) ₂		2106 w	2029 s	2001 m	1965 m

^a Obtained for CCl₄ solutions; each spectrum calibrated against the water vapor band at 1847.7 cm.⁻¹ (5.412 μ). Frequencies for the compounds of manganese and rhenium, heretofore obtained only with sodium chloride optics, have been reported previously by several groups of workers. Some duplicate reported frequencies were found to differ from each other beyond the precision of our instrument and, in the case of the carbonyl iodides, one band less was reported for each pattern than was observed by us. We were compelled to obtain our own comparison spectra for samples of known compounds to establish unambiguously the identity of our compounds of technetium. Full details of these comparisons and discussion of results will appear shortly.

For a solution of 16.5 mg. of I and 0.3 ml. (258 mg.) of toluene (0.13 molal) placed in the inner tube, the separation mentioned above was found to be 14.1 cps. This clearly demonstrates diamagnetic character⁹ and taken together with the data reported above strongly indicates the formula for I as Tc₂(CO)₁₀. The yield of our several preparations was of the order of 7% (based on ammonium pertechnetate). The carbonyl of technetium is analogous to those of its congeners in formula, resembling in its air-sensitivity more the compound of manganese and in its color, that of rhenium.

Technetium carbonyl reacts slowly with iodine at 100° requiring close to 30 hr. to reach completion. In evacuated tubes, or in tubes sealed with one atmosphere of carbon monoxide, reaction proceeded directly to the dimeric product [Tc(CO)₄I]₂. When reactants were held in a sealed capillary tube (i.d., 2 mm.; wall thickness, 3 mm.) in the presence of carbon monoxide at 50 atm., reaction was stopped at the monomeric iodide, Tc(CO)₅I. The course of these reactions, each carried out on 10 mg. of sample, was followed by inspecting the carbonyl stretching region in the infrared for the products. Absorptions, obtained with a Beckman IR 4 instrument equipped with lithium fluoride optics, are listed in Table I for the compounds of technetium as well as those of its congeners.

The nature of the new derivatives synthesized by us is established unambiguously. The known compounds¹ of manganese and rhenium showed patterns of bands closely paralleling in number, position and relative intensities the bands for the compounds of technetium. Fuller details of their properties will be communicated shortly.

Acknowledgment.—The authors are grateful for generous assistance: Ethyl Corp. for a sample of manganese carbonyl; National Science Foundation

(9) A known paramagnetic compound was found to give a separation of 4.8 cps. under the same conditions. This was measured for a 0.092 molal solution of bis-(N-isopropylsalicylaldimine)-Ni(II) in toluene, reported by R. H. Holm and T. M. McKinney (*J. Am. Chem. Soc.*, **82**, 5506 (1960)) to have a magnetic moment of 2.18 BM. in benzene solution, as measured by the Gouy method. We are grateful to Mr. H. F. Bauer of this Department for a sample of the complex, whose magnetic measurements agree with the reported value.

for support through a Science Faculty Fellowship (JCH) and Research Grant G16819 (HDK).

(10) On leave of absence, El Camino College.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CALIFORNIA
LOS ANGELES 24, CALIFORNIA

J. C. HILEMAN¹⁰
D. K. HUGGINS
H. D. KAESZ

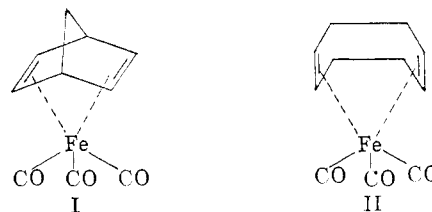
RECEIVED MAY 25, 1961

REARRANGEMENT OF DIENES WITH IRON PENTACARBONYL

Sir:

We wish to report on a new type of reaction involving rearrangement of non-conjugated dienes to corresponding conjugated isomers following treatment with iron pentacarbonyl.

During attempts to extend the series of non-conjugated diene-metal carbonyl derivatives analogous to bicycloheptadiene-iron tricarbonyl (I),^{1,2} equimolar quantities of 1,5-cyclooctadiene and Fe(CO)₅ were heated, with the expectation that the compound of structure II would be formed. Although no stable organo-metallic product was isolated it was found that the 1,5-cyclooctadiene



had been isomerized *quantitatively* to 1,3-cyclooctadiene. Subsequent work has established that catalytic amounts of Fe(CO)₅ will similarly effect complete conversion. Thus, in a typical experiment, 6 g. of Fe(CO)₅ and 94 g. of 1,3-cyclooctadiene were recovered after reaction of 10 g. of Fe(CO)₅ and 100 g. of 1,5-cyclooctadiene at 115° for seven hours. Gas phase chromatographic analysis of samples taken at frequent intervals showed that no organic compound, other than the two dienes men-

(1) R. Pettit, *J. Am. Chem. Soc.*, **81**, 1266 (1959).

(2) R. Burton, M. L. H. Green, E. W. Abel and G. Wilkinson, *Chemistry and Industry*, 1592 (1958).

tioned, was produced in detectable amount at any time during the reaction.

The same isomerization can be effected equally well using bicycloheptadiene-iron tricarbonyl (I), cyclooctatetraene-iron tricarbonyl or hexadiene-iron tricarbonyl in place of $\text{Fe}(\text{CO})_5$. It is significant, however, that the reaction did not occur when 1,3-cyclohexadiene-iron tricarbonyl was used. Furthermore, no rearrangement of 1,5-cyclooctadiene has been observed using $\text{Mo}(\text{CO})_6$, $\text{Cr}(\text{CO})_6$, $\text{Ni}(\text{CO})_4$, $\text{W}(\text{CO})_6$ or methylcyclopentadienylmanganese tricarbonyl, although several of these compounds are reported to form stable 1,5-cyclooctadiene metal carbonyl complexes.³

Reaction of $\text{Fe}(\text{CO})_5$ with other non-conjugated dienes also has effected isomerization of the double bonds to produce conjugated systems, but in most of these cases the product is found to be a stable diene-iron tricarbonyl derivative. Thus, reaction of $\text{Fe}(\text{CO})_5$ and 1,4-cyclohexadiene produced 1,3-cyclohexadiene-iron tricarbonyl, identical with that formed from reaction of 1,3-cyclohexadiene and $\text{Fe}(\text{CO})_5$. Similarly, 1,5-hexadiene and $\text{Fe}(\text{CO})_5$ reacted to produce a mixture of 1,3-hexadiene- and 2,4-hexadiene-iron tricarbonyls. Reactions of $\text{Fe}(\text{CO})_5$ with 4-vinylcyclohexane and *d*-limonene have led to the formation of mixtures of diene-iron tricarbonyl compounds. In each case it has been established, by degradation of the complexes, that the organic ligands in these mixtures are dienes isomeric with the starting materials; determination of the exact composition and structural nature of these mixtures is in progress. It should be noted that Stone and co-workers recently have obtained 1,3-pentadiene-iron tricarbonyl after reaction of 1,4-pentadiene with tri-iron dodecacarbonyl.⁴

Further work dealing with the mechanism and general applicability of this reaction will be reported in full in THIS JOURNAL. We thank the Robert A. Welch Foundation and Alfred P. Sloan Foundation for financial assistance.

(3) E. O. Fischer and W. Frohlich, *Ber.*, **92**, 2995 (1959); M. A. Bennett and G. Wilkinson, *Chemistry and Industry*, 1516 (1959); T. A. Manuel and F. G. A. Stone, *J. Am. Chem. Soc.*, **82**, 366 (1960).

(4) R. B. King, T. A. Manuel and F. G. A. Stone, *J. Inorg. and Nucl. Chem.*, **16**, 233 (1961).

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF TEXAS
AUSTIN 12, TEXAS

J. E. ARNET
R. PETTIT

RECEIVED JUNE 1, 1961

TETRAFLUOROHALATES OF CESIUM, RUBIDIUM AND POTASSIUM¹

Sir:

The interaction of elementary fluorine with CsCl , RbCl or KCl results in the formation of powerful fluorinating agents. These compounds were first investigated by Bode and Klesper who claimed that the compound formed was MF_x where x approaches 3.² They reported that fluorination of CsF , RbF and KF did not produce the "trifluorides" (we concur). These workers claimed

(1) The Los Alamos work was performed under the auspices of the U. S. Atomic Energy Commission and the University of Wisconsin work was supported by the Wisconsin Alumni Research Foundation, the du Pont Company, and the Monsanto Chemical Company.

(2) H. Bode and E. Klesper, *Z. anorg. allg. Chem.*, **267**, 97 (1951).

that it was necessary to start with the alkali chloride, arguing that the molecular volume of the chloride was just the right size to accommodate F_3^- when Cl^- was replaced. *Contrary to the previous work, we find that fluorination of alkali chlorides produces alkali tetrafluorochlorates, MClF_4 , and not the trifluoride, MF_3 .* Our results can be explained by the reaction $\text{MCl} + 2\text{F}_2 = \text{MClF}_4$.

Fluorination of the alkali halides (CsCl , CsBr , CsI , RbCl , RbBr , RbI , KCl , KBr and KI) at temperatures of 15–250° yields primarily the alkali polyfluorohalate. Pure polyfluorohalates are difficult to prepare since the reaction is very exothermic and the decomposition temperature is locally exceeded so that the product usually contains some alkali fluoride. The product occurs as a dense melt.

The most thoroughly studied of these compounds are potassium tetrafluorochlorate and cesium tetrafluorochlorate. These have been prepared by direct fluorination of the alkali chlorides at temperatures from 90–250°. These compounds are white, low melting (*circa* 100–200°) solids which react violently with water to yield primarily chlorate ion rather than chloride (this probably explains the failure of Bode and Klesper to find Cl^-). They also oxidize iodide to iodine and evolve oxygen from the oxidation of water. They decompose to the alkali fluoride and gaseous products upon heating to 350–400° *in vacuo* or in an inert gas stream. The gases evolved upon thermal decomposition of CsClF_4 are ClF and ClF_3 .

X-Ray powder studies of these tetrafluorochlorates show a mixture of the alkali fluoride and a new phase resembling closely, but not exactly, the alkali perchlorate. Infrared absorption bands of KClF_4 , both in KCl discs and in mulls, were found at 1970, 1830, 1225 and 970 cm^{-1} . Magnetic susceptibility studies of CsClF_4 show it to be diamagnetic.

The cesium product was analyzed by oxidation of I^- to I_2 , by weight change occurring on fluorination, and by determination of the total chloride by precipitation of silver chloride after reduction of the chlorate with Na_2SO_3 . The potassium salt was analyzed by iodine titration, by weight loss on heating and by fluoride determination with thorium nitrate.

Bode reported the preparation of strongly oxidizing salts from the fluorination of the alkali bromides and iodides as well as the chloride but did not characterize the products.³ We have prepared the tetrafluorobromates and tetrafluoroiodates of Cs , Rb , and K . The compound CsBrF_4 was obtained almost completely free of CsF . There is some evidence for the existence of CsIF_6 . The rubidium compounds have been studied and the compositions have been determined to be RbClF_4 , RbBrF_4 and RbIF_4 . The potassium compounds are more difficult to prepare in high yield with particular difficulty arising with KI . KBrF_4 has been reported.⁴

Infrared examination of the gases evolved upon thermal decomposition show ClF and ClF_3 from

(3) H. Bode, *Naturwiss.*, **37**, 477 (1950).

(4) A. G. Sharpe and H. J. Emeléus, *J. Chem. Soc.*, 2135 (1948), and A. A. Woolf and H. J. Emeléus, *ibid.*, 2865 (1949).