

TABLE II
OXIDATION OF *l*-MENTHOL AND ISOPINOCAMPHEOL BY VARIOUS PROCEDURES

	Procedure	<i>l</i> -Menthol		Isopinocampheol	
		Products	%	Products	%
1 ^a	Aqueous chromic acid at 50-55°	Menthone	90	Isopinocampheol	86
		Isomenthone	3	Pinocampheol	4
		Menthol	trace	Isopinocampheol	1
2 ^b	Chromic acid in 90% acetic acid at 25°	Menthone	71	Isopinocampheol	78
		Isomenthone	3	Pinocampheol	3
		Menthol	0	Isopinocampheol	0
3 ^c	Chromic acid in acetone at 5-10°	Menthone	86	Isopinocampheol	84
		Isomenthone	4	Pinocampheol	4
		Menthol	2	Isopinocampheol	1
4 ^d	Aqueous chromic acid with alcohol in ether at 25-30°	Menthone	97	Isopinocampheol	94
		Isomenthone	trace	Pinocampheol	trace
		Menthol	1.5	Isopinocampheol	0

^a Ref. 1. ^b Ref. 2. ^c Ref. 3. ^d Present study.

supported by the Office of Ordnance Research. This assistance is gratefully acknowledged.

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RECEIVED MAY 27, 1961

TECHNETIUM CARBONYL

Sir:

We wish to report the synthesis and properties of a new carbonyl, and its derivatives with iodine. This work for technetium fills in the last missing member of the manganese sub-group metal carbonyls which had been more elusive to obtain¹ than those of the neighboring groups. The difficulties were heightened in the case of technetium because of its rarity.

In a typical preparation, ammonium pertechnetate² (0.85 g., 4.70 mmole) was pyrolyzed at 400° in a Vycor tube, the pressure being reduced to 1 mm. after the salt turned black. The contents were then treated with excess dry oxygen at 600°. Upon cooling, the reaction tube containing pale yellow hygroscopic technetium heptoxide was inserted into a copper-plated autoclave (350 ml. capacity), insuring minimum contact with atmospheric moisture. After flushing with 800 psig. of Matheson research grade carbon monoxide, the bomb was pressurized to 3,000 psig./25° and then heated for twenty hours at 220°, pressure rising to 5,100 psig.

After cooling, the autoclave was outgassed slowly through a trap at -78°. Only traces of material later identified as the carbonyl were found in the trap, but, in particular, no evidence in the infrared (4,000-650 cm.⁻¹) was obtained which might have indicated volatile Tc-H containing materials.³ The autoclave and contents were rinsed with diethyl ether which subsequently was evaporated at water

pump vacuum. A residue was deposited which upon sublimation (50°, 10⁻²mm.) yielded 50-100 mg. of colorless crystals (I). There was evidence of some decomposition when solutions of this product were extensively handled in air, in accordance with the behavior of some other metal carbonyls, particularly that of manganese. Recrystallization from pentane followed by two sublimations yielded material which melted (sealed capillary) at 159-160° (corr.). The spectrum of I in the carbonyl stretching region of the infrared consisted of three bands, listed in the table below, closely paralleling in position and intensity those of Mn₂(CO)₁₀ and Re₂(CO)₁₀.

Analysis of I for carbon monoxide was carried out on the vacuum line by slowly heating 46.8 mg. of compound, below the softening point of Pyrex glass. Carbon monoxide thus evolved was identified by infrared spectrum: found, 21.5 cc.⁴; required for [Tc(CO)₅]_n, 21.9 cc.

In a micromolecular weight apparatus adapted to high vacuum techniques from that described by Gysel, *et al.*,⁵ 12.5 mg. of I was mixed with 300.9 mg. of diethyl ether resulting in a vapor pressure depression of 3.08 mm. at 22°. Molecular weight: required for Tc₂(CO)₁₀, 478; found,⁶ 465 ± 26.

Magnetic susceptibility for I was determined by nuclear magnetic resonance, using the method described by Evans,⁷ adapted by us for use with coaxial sample tubes of Zimmerman and Foster.⁸ The separation for neat liquids between the resonance of methyl protons of toluene in the inner tube and protons of cyclohexane in the annular space was found to be 13.3 cps. at 40 mc. and 31°.

(4) All cc. are given for S.T.P.

(5) H. Gysel, W. Padowetz and K. Hamberger, *Mikrochim. Acta*, 192 (1960).

(6) Accuracy of our method, to be fully described in a forthcoming paper, depends on tensimetric homogeneity of solvent. Need for accurate temperature measurement or for reproducing vapor pressures quoted for the solvent in the literature is avoided. Actual vapor pressure of solvent is measured during molecular weight run, in the same constant temperature bath. For the measurement reported here, diethyl ether, purified by distillation from LiAlH₄, exerted a vapor pressure of 468 mm. (handbook value, 462 mm.). Tensimetric homogeneity was demonstrated for two successive 0.5 ml. samples as no difference in vapor pressure was noted to within 0.02 mm.

(7) D. F. Evans, *J. Chem. Soc.*, 2003 (1959).

(8) J. R. Zimmerman and M. R. Foster, *J. Phys. Chem.*, 61, 282 (1957).

(1) (a) J. Chatt, P. L. Pauson and L. M. Venanzi, Chapter 10, A.C.S. Monograph 147, "Organometallic Chemistry" (Editor, H. Zeiss), Reinhold Publishing Corp., New York, N. Y., 1960; (b) H. E. Podall, *J. Chem. Ed.*, 38, 187 (1961).

(2) Technetium, synthetically produced, consisting mainly of isotope ⁹⁹Tc, *t*_{1/2} = 2.12 × 10⁵ y., β = 0.29 mev., is obtained as NH₄TcO₄ from Oak Ridge National Laboratories, Oak Ridge, Tenn.

(3) Re(CO)₅H has been isolated in the preparation of rhenium carbonyl from the heptoxide or the heptasulfide for cases where the starting material was known not to be rigorously dry, cf. W. Hieber and H. Fuchs, *Z. anorg. Chem.*, 248, 256 (1941).

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).

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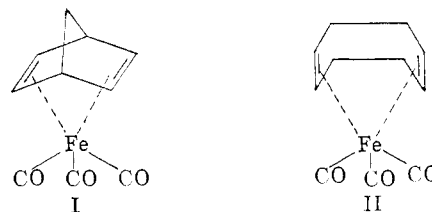
RECEIVED MAY 25, 1961

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).