# NOTIZEN

## Reaction of Group VI Metal Carbonyls with Diphenyliodonium Salts

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DAVIDSON and DYER [1] have shown that diphenyliodonium salts can give carbonyl insertion products when treated with carbon monoxide under pressure, e. g.,

$$(C_6H_5)_2I^{\oplus}NO_3^{\ominus}+CO\xrightarrow[100-110^{\circ}]{CH_3OH}C_6H_5COOCH_3+C_6H_5COOH\,.$$

As part of an investigation of the reactions of metal carbonyls with different functionalities [2], it was of interest to determine whether carbonyl insertion products could be obtained, in synthetically useful yields, by the use of Group VI metal carbonyls as reagents.

Reaction of molybdenum or tungsten hexacarbonyl with diphenyliodonium chloride, bromide, and iodide in dry 1,2-dimethoxyethane or a mixture of the ether and toluene gave air-stable halopentacarbonylmetal anions (Table I).

$$(C_6H_5)_2I^{\oplus}X^{\ominus}+M(CO)_6\rightarrow (C_6H_5)_2I^{\oplus}[M(CO)\,X]^{\ominus}+CO\,.$$

$$X=Cl,\,Br,\,I\quad M=Mo,\,W$$

Analogous complexes have been obtained by reaction of Group VI metal carbonyls with N-methylpyridinium iodide [3], tetraalkylammonium halides [4], and alkali-metal iodides (in diglyme) [5]. Chromium hexacarbonyl did not react with diphenyliodonium bromide or iodide under the described conditions.

| $(C_6H_5)_2I^{\oplus}[M(CO)_5X]^{\ominus}$ M= | X= | Color | $\nu(C\equiv O)$ [b] [cm$^{-1}$] |
|---|---|---|---|
| Mo | Cl | Yellow | 2064 (w), 1904 (s), 1853 (m) |
| Mo | Br | Yellow-green | 2064 (w), 1927 (s), 1855 (m) |
| Mo | I | Yellow-brown | 2067 (w), 1968 (sh), 1902 (s), 1853 (m) |
| W | Br | Yellow-brown | 2065 (w), 1881 (s), 1850 (m) |
| W | I | Yellow | 2066 (w), 1952 (sh), 1885 (s), 1836 (m-s) |

Table I. Infrared Terminal Metal Carbonyl Stretching Frequencies for Complexes of Type $(C_6H_5)I^{\oplus}[M(CO)_5X^{\ominus}$.
[a] Abbreviations: s, strong; m, medium; w, weak; sh, shoulder.
[b] KBr disc.

In the infrared spectra, the terminal metal carbonyl stretching frequencies for the diphenyliodonium complexes (Table I) are generally similar to the values reported for the corresponding tetraalkylammonium complexes [4] (all spectra recorded as KBr discs), except that the E and $A^{1a}$ bands appear at a lower frequency for the iodonium compounds. The difference in position of these bands may be due to the different size and shape of the diphenyliodonium as compared to the tetraalkylammonium ion (polarization effects).

Reaction of diphenyliodonium nitrate with molybdenum hexacarbonyl gave a brown solid showing terminal metal carbonyl stretching bands in the infrared at 2066 (w), 2010 (s), and 1912 (s) cm$^{-1}$ (KBr). The product may be $(C_6H_5)_2I^{\oplus}[Mo(CO)_5NO_3]^{\ominus}$ but a satisfactory elemental analysis could not be obtained.

### Experimental Section

Chromium hexacarbonyl was purchased from Pressure Chemical Company. Molybdenum and tungsten hexacarbonyls were generously supplied by Climax Molybdenum Company. Diphenyliodonium chloride, iodide and nitrate were purchased from Aldrich Chemical Company and the bromide was obtained from Eastman Organic Chemicals. Elemental microanalysis were performed by A. BERNHARDT, Fritz-Pregl-Straße, Mülheim/Ruhr, West Germany. Satisfactory ($\pm 0.4\%$) C, H, I and metal elemental analyses were obtained for all new compounds except for the product resulting from the diphenyliodonium nitrate reaction. Infrared spectra were recorded on a Perkin-Elmer 521 spectrophotometer; polystyrene film was used for calibration purposes. All reactions were run in a nitrogen atmosphere.

*General Procedure.* A mixture of the diphenyliodonium salt (0.5 – 0.7 g) and excess metal hexacarbonyl in dry 1,2-dimethoxyethane (25 ml, $(C_6H_5)_2I^{\oplus}Br^{\ominus}$ – $Mo(CO)_6$ reaction) or 1,2-dimethoxyethane-toluene (10 : 14 ml, all other reactions) was heated with stirring at 90 – 115° (oil bath temperature) for 1.5 – 4.0 hours. The solution was filtered hot and *n*-pentane was then added to the cooled filtrate. The resulting precipitate was filtered, washed twice with *n*-pentane, and dried. Any unreacted metal hexacarbonyl was removed by sublimation.

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