TABLE I

4-HYDROXY-3-METHOXYPHENYLALKYLCARBINOLS

					Diacetyl derivatives					
Alkyl group	Yield, %	M. p., °C.	Methoxyl, %		B. p.,[a] °C.	M. p., °C.	Methoxyl, %		Acetyl, %	
			Calcd.	Found			Calcd.	Found	Calcd.	Found
Ethyl	68	84–85	17.0	17.0	116–118	48–49	11.7	11.5	32.4	31.9
n-Propyl	50	61.5–62.5	15.8	15.8	120–121	1.5054[d]	11.1	11.1	30.7	30.7
Isopropyl	46	86.5–87	15.8	15.7	117–119	52–53	11.1	10.9	30.7	31.2
n-Butyl	57	80.5–81[b]	14.7	14.8	128–131	1.5023[d]	10.5	10.6	29.2	29.2
s-Butyl	30	64.5–65	14.7	14.9	122–124	1.5041[d]	10.5	10.3	29.2	30.2
t-Butyl	67	73–73.5	14.7	14.6	118–120	82–83	10.5	10.4	29.2	29.0
Isobutyl	32	51–53	14.7	15.0	122–123	1.5020[d]	10.5	10.7	29.2	29.6
n-Amyl	51	76.5–77.5	13.8	13.7	135–137	1.4998[d]	10.1	10.3	27.9	27.9
Ethyl[c]	88	89.5–90[c]	11.9	11.8						

[a] At 0.2 mm. [b] Reported value: 81.5°.[5] [c] 5-Bromo-4-hydroxy-3-methoxyphenylethylcarbinol, reported m. p., 88–89°. [d] $n^{20}D$.

ular quantity of methylmagnesium iodide involved only the phenolic hydrogen. Recently Cartwright and Haworth[6] prepared 1-(5-bromo-4-hydroxy-3-methoxyphenyl)-1-propanol by treating a fivefold excess of ethylmagnesium iodide with 5-bromovanillin. Duplication of their procedure led to an 88% yield.

The alcohols listed in Table I were prepared by treating vanillin with approximately six equivalents of the appropriate alkylmagnesium bromide in the usual manner. The presence of two hydroxyl groups (one on the phenyl residue and one on the side chain) was shown by the preparation of the diacetyl derivative. When three equivalents of alkylmagnesium bromide was used the yields were about 5% lower than those given in the Table.

The 1-(3,4-dimethoxyphenyl)-1-alkanols shown in Table II were obtained from the treatment of veratraldehyde with 2 equivalents of the corresponding alkylmagnesium bromides. Analysis of the products for hydroxyl gave low results and several attempts to obtain crystalline esters or urethans were unsuccessful. The principal reaction with excess phenyl isocyanate at 100° was dehydration evidenced by the formation of diphenylurea in good yields.

TABLE II

3,4-DIMETHOXYPHENYLALKYLCARBINOLS

Alkyl group	Yield, %	B. p.,[a] °C.	$n^{20}D$ or m. p., °C.	Methoxyl, % Calcd.	Methoxyl, % Found
Ethyl	62	102–103	1.5525	31.7	31.6
n-Propyl	63	110	64–65	29.6	29.6
Isopropyl	75	103	63–64[b]	29.6	29.5
n-Butyl	52	120–123	1.5395	27.6	27.4
s-Butyl	48	110–112	47–48[c]	27.6	27.4
Isobutyl	46	114–116	1.5355	27.6	27.8

[a] At 0.2 mm. [b] $n^{20}D$ 1.5403. [c] $n^{20}D$ 1.5357.

Experimental

The Grignard reactions were run in the usual manner. The preparation of 1-(4-hydroxy-3-methoxyphenyl)-1-propanol is typical. Magnesium turnings (9.5 g., 0.39 mole) and a crystal of iodine were placed in a dry 3-necked flask. Seventy-five cc. of absolute ether and 5 g. of ethyl bromide were added. When the reaction commenced a solution of 37.5 g. of ethyl bromide (0.39 mole total) in 75 cc. of ether was added dropwise with stirring during one hour and stirring was continued an additional one-half hour. The yield of ethylmagnesium bromide, determined by titration,[7] was 0.36 mole (94%). A solution of 10.0 g. (0.066 mole) of vanillin in 200 cc. of ether was then added dropwise during 1.25 hours, the resulting suspension was stirred an additional 1.75 hours and allowed to stand overnight. Saturated ammonium chloride solution (300 cc.) was then added and the mixture stirred until decomposition of the bromomagnesium salt was complete. After separating the ether layer, the aqueous layer was washed three times with ether. The ether solutions were combined, dried over magnesium sulfate and evaporated at aspirator pressure to approximately 50 cc. When this solution was poured into 300 cc. of petroleum ether, an oil separated and crystallized upon standing. Filtering and drying gave 8.2 g. (68%) of crude product, m. p. 79–84°. Purification was effected by recrystallizing from benzene or benzene–petroleum ether mixtures. The diacetates were obtained using excess acetic anhydride in pyridine solution at room temperature.

The 3,4-dimethoxyphenylalkylcarbinols were prepared in similar manner. The bromomagnesium salt (from 0.6 mole magnesium, 0.6 mole alkyl bromide and 0.3 mole veratraldehyde) was decomposed by pouring the reaction flask contents into a mixture of 500 g. of ice and 40 ml. of concentrated sulfuric acid. The *n*-propyl- and isopropylcarbinols were obtained crystalline from the ether–petroleum ether precipitation and were purified either by recrystallization or distillation. The other carbinols were oils and were purified by distillation at 0.2 mm. pressure.

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(6) Cartwright and Haworth, *J. Chem. Soc.*, 535 (1944).

(7) Gilman, Zoellner and Dickey, THIS JOURNAL, **51**, 1580 (1929). The yields in the other cases were also in close agreement with those reported by these authors.

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The Infrared Spectrum and Structure of Tungsten Carbonyl

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X-Ray diffraction studies[1] of the solid hexacarbonyl of tungsten and electron diffraction studies[2] of its vapor indicate with reasonable certainty that the six carbonyl groups are arranged octahedrally around the central tungsten atom as shown in Fig. 1. This structure can also be inferred from the fact that $W(CO)_6$ is a complex with a coördination number of 6 which hybridizes two 5d, one 6s and three 6p orbitals, the d^2sp^3 hybrid being an octahedron.

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(1) W. Rüdorff and U. Hofmann, *Z. physik. Chem.*, **B28**, 351 (1935).

(2) L. O. Brockway, R. V. G. Ewens and M. W. Lister, *Trans. Faraday Soc.*, **34**, 1350 (1938).

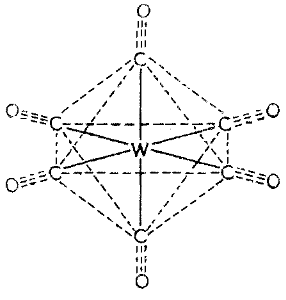

Fig. 1.

It would be interesting to see if the infrared spectrum of $W(CO)_6$ agrees with this structure. Further, the nature of the bonding in the metal carbonyls is not thoroughly established.[3] In particular, the carbon oxygen bonds may be like that in carbon monoxide or they may be like that of an organic ketone or aldehyde. Accordingly, the infrared spectrum of $W(CO)_6$ was taken in the region from 2 to 15 μ. The spectrum is shown in Fig. 2. Since there were no peaks in the region 8–15 μ, the spectrum is not presented for this region. The broad unresolved adsorption band from 5000 to 2300 cm.$^{-1}$ is probably due to especially strong scattering because the solid particles of $W(CO)_6$ are of approximately the same size, at the wave length of the infrared light in the region from 5000 to 2300 cm.$^{-1}$. The anomalously high transmission in the region around 2080 cm.$^{-1}$ is undoubtedly due to the Christiansen filter effect.[4,5] Of all the fundamental infrared active frequencies to be expected in the 13 atom octahedral system, $W(CO)_6$, only the unsymmetrical stretchings of C–O would be expected in the region 2–15 μ. All the other modes would lie in the longer wave length region. One would expect a stretching for the polar C–O's and a stretching for the equatorial C–O's. These two stretchings should be quite similar. It is, therefore, not surprising that the infrared spectrum is so simple. The single band at 1997 cm.$^{-1}$ is undoubtedly the CO stretching. The fact that two bands are not resolved is not particularly disturbing since infrared spectra of solids usually give poor resolution. Thus, for example, the two carbon monoxide-like frequencies in solid $Fe_2(CO)_9$ were barely resolved.[6]

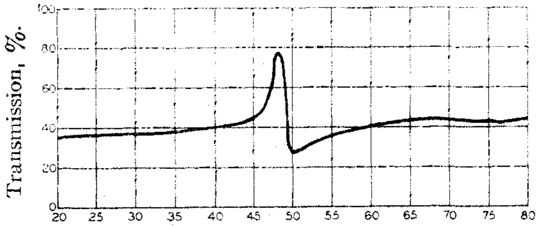

Fig. 2.—Solid state infrared spectrum of tungsten carbonyl $W(CO)_6$.

It has been suggested that the bond character of the metallic carbonyl is a hybrid,[2] or one of the extremes,[3] of the structure

$$M \leftarrow C \equiv O \qquad M = C = O$$
(a) (b)

The structure of the compounds is determined by a single bond (a above) hybridization scheme. This does not preclude the possibility of certain amounts of (b) in the structure. It has been known for a long time that the composition of the metallic carbonyls is determined by the condition that the effective atomic number of the metallic central atom be increased to that of the next inert gas. The fact that all the mono-metallic carbonyls fit into this system argues for the equivalence of the carbonyl groups. This equivalence is also shown in Table I in which C–O distances and C–O stretching frequencies are given. The equivalence of both the bond lengths and stretching frequencies is striking. Furthermore, it is to be noted that the comparison of distances and stretching frequencies indicates the CO in metallic carbonyls is very much nearer that of carbon monoxide than those of the average ketone or aldehyde. Accordingly, it may be reasonably certainly concluded that in the mono-metallic carbonyls a little modified carbon monoxide is coördinately bonded to a central metal atom.

TABLE I

STRETCHING FREQUENCIES AND INTERATOMIC DISTANCES IN THE C–O (CARBON MONOXIDE TYPE) BOND IN METAL CARBONYLS

Compound	C–O distn., Å.	C–O stretching frequencies, cm.$^{-1}$
$Ni(CO)_4$	1.15	2039, 2050
$Fe(CO)_5$	1.15	1994, 2028
$Fe_2(CO)_9$	1.15	2034, 2080
$Fe_3(CO)_{12}$	. .	2020, 2043
$W(CO)_6$	1.13	1997
$Cr(CO)_6$	1.15	. .
$Mo(CO)_6$	1.15	. .
CO (carbon monoxide)	1.13	2155
CO (in average ketone or aldehyde)	~1.25	~1750

Experimental Part

The tungsten carbonyl was obtained from the A. D. McKay Company. It was used directly without further purification. Because it was relatively insoluble in solvents which have appreciable windows in the infrared, it was necessary to obtain the spectrum of $W(CO)_6$ in the solid state. The crystals were ground into a fine powder of average particle size ~ 1 μ. It was then spread over a potassium bromide plate in a uniform film. The infrared spectrometer was the Perkin-Elmer 12B automatically recording prism spectrometer utilizing sodium chloride optics.

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(4) R. B. Barnes and L. G. Bonner, *J. Opt. Soc. Am.*, **37**, 713 (1947).

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