1.30 ml. of water. Then 0.0638 g. of the *aci*-nitro compound was dissolved in 7.5 ml. of the buffer solution. At the end of 15 minutes at room temperature the reaction mixture was diluted with 20 ml. of water, ether extracted, and the extracts washed with bicarbonate and then water. The dried extracts on concentration yielded material analyzing with quantitative infrared for 98% *cis*-1-nitro-2-phenylcyclohexane and free of carbonyl impurity.

Equilibration of the 1-Nitro-2-phenylcyclohexanes.—To 50 ml. of 95% ethanol was added 50 mg. of sodium bicarbonate and the mixture was heated to boiling; the saturated solution was decanted from undissolved solid. To 5.0 ml. of the saturated bicarbonate solution was added 45 mg. of *cis*-1-nitro-2-phenylcyclohexane. The solution was refluxed for four hours. Dilution with water followed by ether extraction, drying and concentration led to the equilibrated mixture which was analyzed by quantitative infrared. This indicated 99% *trans* isomer. Similar equilibration of the *trans* isomer gave a mixture containing 1% *cis* isomer and 99% *trans*.

The solubility of sodium bicarbonate in hot 95% ethanol (*ca.* 1 mg./25 ml.) was low enough to ensure the presence of only catalytic quantities.

Quantitative infrared analyses were performed by the method described previously.[5] The analytical wave lengths were 11.11 μ, characteristic of the *trans* isomer, and 11.92 μ, characteristic of the *cis* compound. All runs were made in chloroform in 0.10-mm. cells at a total concentration of 40 mg./0.20 ml. of solvent.

EVANSTON, ILLINOIS

COMMUNICATIONS TO THE EDITOR

TRIPHENYLCHROMIUM[1]

Sir:

We wish to report the preparation and properties of the first isolable[2] member of a series of covalent organo-chromium compounds, **triphenylchromium,** $(C_6H_5)_3Cr(III)$.[3] This blood-red crystalline substance is deposited from tetrahydrofuran, after reaction of chromic trichloride and phenylmagnesium bromide in a mole ratio of 1:3 at −20° in the same solvent, as a tetrahydrofuranate $(C_6H_5)_3Cr(THF)_3$ (I) (*Anal.* Calcd.: Cr, 10.4. Found: Cr, 10.2), or combined with magnesium halide tetrahydrofuranate, $(C_6H_5)_3Cr(THF)_3 \cdot 3[MgBrCl(THF)]$ (II) (*Anal.* Calcd.: Cr, 4.58. Found: Cr, 4.62), depending upon the initial concentration of the reactants. The magnesium salt may be removed from II by diluting a tetrahydrofuran solution of II with diethyl ether which causes concurrent separation of I from the solution.

I and II are chemically similar in that they are inordinately sensitive to moisture, hydrolyzing instantaneously to green $Cr(H_2O)_6^{+++}$. In tetrahydrofuran solution they are cleaved rapidly by mercuric chloride and yield quantitatively three moles of pure phenylmercuric chloride, m.p. 266–267°, for each chromium atom present in I or II (*Anal.* 2.29 g. (2.02 mmoles) of II yields 1.94 g. (6.19 mmoles) of C_6H_5HgCl and 0.105 g. (2.02 mmoles) of Cr^{+++}. Calcd.: C_6H_5/Cr, 3/1; C_6H_5, 20.4; Cr, 4.58. Found: C_6H_5/Cr, $3.0_6/1$; C_6H_5, 20.8; Cr, 4.58), the red color of $(C_6H_5)_3Cr(THF)_3$ in either case changing to the violet color of $Cr(THF)_6^{+++}$. A sample of II has been found to be strongly paramagnetic to the extent of 3.89 Bohr magnetons in agreement with a chromium valency of 3.[4]

Further evidence for the identities of I and II is derived from the loss of tetrahydrofuran from these substances either by heating at atmospheric pressure, by vacuum at room temperature or by washing with diethyl ether. II loses 39.3% of its weight, corresponding to a loss of 6 moles (38.0%) of tetrahydrofuran, while I gives up 41.5% or 3 moles (43.3%) of tetrahydrofuran per mole of formula molecular weight. In both instances the red color of I and II is lost also, and a black solid is formed (from II, admixed with white magnesium salt) which on hydrolysis under nitrogen with oxygen-free water yields **bis-benzenechromium(0)** and **benzene-biphenylchromium(0)** directly in approximately equal amounts. Air oxidation of a benzene solution of these complexes permits their transference to aqueous solution as cations and precipitation as tetraphenylborates for yield and further identity determinations.

The rearrangement of I and II in diethyl ether to the completely reduced forms of the chromium complexes, showing that triphenylchromium has a short life in this solvent, has led to a re-examination of the original Hein reaction between chromic trichloride and phenylmagnesium bromide in diethyl ether.[5] The primary products of this reaction, after hydrolysis *under nitrogen*, are found to be the same completely reduced complexes. This remarkable rearrangement of a covalently bonded structure to that of a π-complex will be the subject of forthcoming papers.

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(1) Paper IV, "π-Complexes of the Transition Metals"; Paper III, M. Tsutsui and H. H. Zeiss, *Naturwissenschaften*, **44**, 420 (1957).

(2) F. A. L. Anet and E. Leblanc, THIS JOURNAL, **79**, 2649 (1957), report the existence of $Cr(H_2O)_5CH_2Ph^{++}$ in solution.

(3) This term was first applied by F. Hein and E. Markert, *Ber.*, **61**, 2255 (1928), to the compound now recognized to be benzenebiphenylchromium(0).

(4) We are indebted to Dr. R. B. Johannesen of the National Bureau of Standards, Washington, D. C., for this and other magnetic measurements.

(5) H. H. Zeiss and M. Tsutsui, THIS JOURNAL, **79**, 3062 (1957).

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RECEIVED NOVEMBER 15, 1957

FLAVONOIDS OF CITRUS. II. ISOLATION OF A NEW FLAVONOL FROM LEMONS

Sir:

The enzymatic (hemicellulase) hydrolysis of a preparation[1] of the flavonoid glycosides of lemon peel affords a complex mixture of aglycones.

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(1) "Calcium Flavonate Glycoside, Lemon," purchased from Sunkist Growers, Ontario, California. The use of this material is not intended as an endorsement by the Department of Agriculture.

The ether-insoluble fraction of this mixture consists largely of eriodictyol (m.p. 271°), the presence of which in lemons has now been established unequivocally. The ether-soluble fraction contains a number of other aglycones which, upon standing, deposit a small quantity of a crystalline, chromatographically homogeneous flavonol, m.p. 274–275°, λ_{max} 259 and 378 mμ. Analytical data for the compound (Calcd. for $C_{17}H_{14}O_8$: C, 59.0; H, 4.08; CH_3O, 17.9. Found: C, 58.8; H, 4.27; CH_3O, 18.7), its tetraacetate (m.p. 155–156°; calcd. for $C_{25}H_{22}O_{12}$: C, 58.4; H, 4.31; CH_3O, 12.1. Found: C, 58.3; H, 4.37; CH_3O, 12.4) and its tetra-ethyl ether (m.p.[2] 116 and 130°; calcd. for $C_{25}H_{30}O_8$: C, 65.4; H, 6.59; CH_3O, 40.6. Found: C, 65.6; H, 6.68; CH_3O, 40.9) establish it as a dimethoxytetrahydroxyflavone. Methylation with excess methyl sulfate yields gossypetin hexamethyl ether (3,5,7,8,3′,4′-hexamethoxyflavone) (m.p.[2] and mixed m.p. 148–150° and 168–169°), while methylation with three moles of methyl sulfate yields 5-hydroxy-3,7,8,3′,4′-pentamethoxyflavone (m.p. and mixed m.p. 156–157°). The compound is, therefore, a dimethyl ether of gossypetin having a free 5-hydroxy group. It is the first representative of this flavonol to be found in citrus and has been named *limocitrin*.

The location of one of the methoxy groups at the 3′-position is proved by the isolation of vanillic acid from the alkaline cleavage products. That the other methoxy group must be located at the 8-position is shown by the facts that limocitrin, unlike flavones containing a free 5,8-dihydroxy group, does not undergo aerial oxidation to deeply colored substances in alkaline solution and fails to give the gossypetone reaction when treated with *p*-benzoquinone in alcohol. It follows that the structure of limocitrin is 3′,8-dimethoxy-3,5,7,4′-tetrahydroxyflavone.

This structural assignment has been confirmed by various spectral measurements. Thus, a free 7-hydroxy group is indicated by the shift of the short wave length band from 259 to 282 mμ in the presence of sodium acetate,[3] while a free 3,4′-dihydroxy group is indicated by the disappearance of the long wave length band in 0.002 *N* sodium ethoxide solution.[3] The absence of an *o*-dihydroxy group is shown by the failure of the bands to shift in the presence of boric acid–sodium acetate.[4] The structure suggested is the only dimethyl ether of gossypetin which can accommodate these spectral data.

The identification of other aglycones in the mixture is in progress.

[2] Double melting point.

[3] L. Jurd and R. M. Horowitz, *J. Org. Chem.* (in press).

[4] L. Jurd, *Arch. Biochem. Biophys.*, **63**, 376 (1956).

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A NEW AND SELECTIVE METHOD OF OXIDATION

Sir:

We have found that the oxidation $\rangle C\langle\begin{smallmatrix}H\\Br\end{smallmatrix} \rightarrow \rangle C{=}O$ can be achieved simply by dissolving the halide in dimethyl sulfoxide. In the majority of cases studied thus far the reaction proceeds at room temperature. Table I summarizes our findings. Extension of this reaction is being explored as is also the matter of mechanism.

TABLE I

OXIDATION OF >CHBr to >C=O

Halide	Product	Yield, %
$C_6H_5COCH_2Br$	C_6H_5COCHO	71
p-Br-C_6H_4-$COCH_2Br$	*p*-Br-C_6H_4-COCHO[a]	84
p-Cl-C_6H_4-$COCH_2Br$	*p*-Cl-C_6H_4-COCHO	69
p-C_6H_5-C_6H_4-$COCH_2Br$	*p*-C_6H_5-C_6H_4-COCHO[a]	85
p-NO_2-C_6H_4-$COCH_2Br$	*p*-NO_2-C_6H_4-COCHO	72
$C_6H_5CHBrCOC_6H_5$	$C_6H_5COCOC_6H_5$[b]	95
p-NO_2-C_6H_4-CH_2Br	*p*-NO_2-C_6H_4-CHO	48

[a] Isolated as the hydrate. [b] At 45° for 44 hours.

As a typical example: *p*-bromophenacyl bromide (15.98 g.) is dissolved in 100 ml. of dimethyl sulfoxide at room temperature. After nine hours the solution is poured into ice-water and extracted with diethyl ether; the extracts are washed with water and dried over anhydrous magnesium sulfate. Removal of the ether *in vacuo* yields 14.6 g. of a slightly pasty, pale yellow, solid. One recrystallization from ethyl *n*-butyl ether gives 11.2 g. (84% yield) of white needles, m.p. 123–124°. *Anal.* Calcd. for $C_8H_5O_2Br \cdot 0.5\ H_2O$: C, 43.27; H, 2.72; Br, 35.90. Found: C, 43.58; H, 2.87; Br, 35.73. This hydrate is quantitatively converted to the hemi-acetal (m.p. 62–63°) by dissolving it in hot absolute ethanol and evaporating the solution to dryness *in vacuo*. *Anal.* Calcd. for $C_8H_5O_2Br$-C_2H_5OH: C, 46.3; H, 4.25; Br, 30.8. Found: C, 46.2, 46.2; H, 4.28, 4.32; Br, 30.9; 30.9. The glyoxal hydrate gives a *bis*-semicarbazone: m.p. 253–254°. *Anal.* Calcd. for $C_{10}H_{11}BrN_6O_2$: C, 36.71; H, 3.39. Found: C, 36.91; H, 3.46.

Periodic acid oxidation of *p*-bromophenyl glyoxal results in a 98% yield of *p*-bromobenzoic acid and an 88% yield of formic acid. In contrast, from the keto alcohol *p*-BrC_6H_4-CO-CH_2OH, on treatment with periodic acid, an 87% yield of *p*-bromobenzoic acid and a 61% yield of formaldehyde is obtained.

The foregoing simple procedure is not satisfactory with benzyl bromides. However, by raising the temperature, and using acetonitrile as a solvent, pure *p*-nitrobenzaldehyde has been obtained in 48% yield from *p*-nitrobenzyl bromide.

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[1] Under Contract No. AF 18 (600)–310 monitored by the Office of Scientific Research, Air Research and Development Command.

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