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 $(C_6H_5)_3$-$Cr(THF)_3$ (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.

[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 benzene-biphenylchromium(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.

[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.