of podophyllotoxin. The method also indicates the feasibility of synthesizing base-sensitive podophyllotoxin derivatives, of interest in connection with cancer chemotherapy, *via* the stereochemically stable picropodophyllin forms.

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POLY-[DI-μ-DIPHENYLPHOSPHINATO-ACETYLACETONATOCHROMIUM(III)]. A COÖRDINATION POLYMER WITH AN INORGANIC BACKBONE

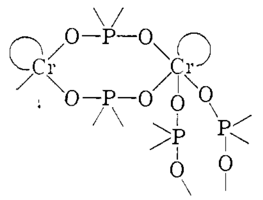
Sir:

Much of the recent activity directed toward the synthesis of coördination polymers has involved the investigation of systems in which metallic ions are catenated by bis-chelating agents.[1-11] Such catenating groups are, *perforce*, organic in nature, with the result that the backbone of the polymer contains organic linkages. At this time we wish to report the preparation of a new kind of coördination polymer with a completely inorganic backbone.

By a substitution–addition polymerization,[12] we have made a series of products with the basic composition $Cr(AcCHAc)(OPPh_2O)_2$. Although we have produced such products by several techniques, the most satisfactory has been the direct reaction between chromium(III) acetylacetonate and diphenylphosphinic acid at temperatures from 175 to 250° under a slow sweep of nitrogen. Heating is continued until acetylacetone can no longer be detected in the exit gas by reaction with ferric ion. The residue then is separated into fractions by extracting successively with ethanol, benzene, and chloroform in a Soxhlet extractor. After these extractions the amount of insoluble residue from the reaction between 10.5 g. of $Cr(AcCHAc)_3$ and 13.1 g. of $Ph_2P(O)OH$ was 2.7 g. at 175°, 5.8 g. at 200°, and 9.4 g. at 250°, a marked increase with increasing temperature. A fraction insoluble in ethanol but soluble in benzene contained 9.4% Cr, 9.3% P, 58.5% C, and 4.9% H; a fraction insoluble in ethanol and benzene but soluble in chloroform 8.6% Cr, 10.8% P, 59.6% C, and 4.8% H; a fraction insoluble in all three 8.6% Cr, 10.3% P, 59.1% C, and 4.9% H. The latter two agree well with 8.88% Cr, 10.58% P, 59.49% C, and 4.65% H, the values calculated for $[Cr(AcCHAc)(OPPh_2O)_2]_n$; the former with the values 9.66% Cr, 9.21% P, 58.46% C, and 4.83% H calculated for $(AcCHAc)[Cr(AcCHAc)(OPPh_2O)_2]_4Cr(AcCHAc)_2$.

Ebullioscopic measurements in benzene have yielded number-average molecular weights of 1940 to 2633 for benzene-soluble fractions and up to 10,870 for chloroform-soluble fractions. The benzene-soluble fraction thus contains on the average four to five chromium-containing units per polymer segment assuming either acetylacetonate or diphenylphosphinate end groups, the chloroform-soluble, about eighteen. We have not been able to determine the molecular weight of the insoluble fractions yet, but, since some of the soluble as well as the insoluble fractions have compositions agreeing with the infinite polymer, the difference between them presumably is one of molecular weight, the less soluble fractions having higher molecular weights. It thus appears that we have succeeded in forming a polymer with degree of polymerization dependent upon reaction conditions, substantially greater amounts of higher molecular weight species forming at higher reaction temperatures.

The structure of these polymers probably involves double diphenylphosphinate bridges[13] between chromium atoms in the backbone, *i.e.*



Strong evidence for such an assumption is afforded by the isolation and characterization of the first member of the series, the dimer $(AcCHAc)_2Cr(OPPh_2O)_2Cr(AcCHAc)_2$. It is readily produced in high yield by the reaction of diphenylphosphinic acid with excess chromium(III) acetylacetonate at 240°, gives proper analysis for the formula given (found 11.0% Cr, 6.5% P, 56.7% C, and 5.2% H; calcd. 11.13% Cr, 6.63% P, 56.54% C, and 5.16% H), and gives an ebulliometric molecular weight of 917 in benzene (calcd. 934.8). Increasing the relative amount of diphenylphosphinic acid results in the continuation of the chain started in the dimer, building up a polymer of $Cr(AcCHAc)(OPPh_2O)_2$ units. An alternate technique we have used for the preparation of the polymer is the reaction of the dimer with diphenylphosphinic acid in 1:2 ratio.

An examination of the structure of the polymer with Stuart–Briegleb models shows that closure of a ring requires several units and is unlikely.

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Furthermore, the fact that a number of different fractions is isolated argues against simple ring formation in this reaction. A preliminary infrared examination of the different fractions also supports the thesis that there are species with different molecular weights present. In general the spectra are similar, but there are differences in the PO_2 absorption bands that are suggestive. The PO_2 absorption bands for the dimer and for diphenylphosphinic acid in the region 1100–1230 cm.$^{-1}$ are fairly sharp, whereas in the various products described here there appear to be several overlapping absorptions lying above and below the location of the corresponding PO_2 absorption in the dimer and in diphenylphosphinic acid. This suggests the presence of a mixture of different polymeric species with the PO_2 absorption band shifted to various positions depending on its environment. Preliminary confirmation for such a sensitivity is afforded by the observation of a frequency shift for this absorption maximum when the acetylacetonate group in the dimer is replaced by another chelating ligand.

Thermogravimetric analysis gives a temperature of 296–300° for initial weight loss for the insoluble fraction and 336° for initial weight loss of a fraction soluble in benzene. Since chromium(III) acetylacetonate has been found to start decomposing at an appreciable rate at 250°,[14] it is most likely that the weakest spot in the structure is at the acetylacetonate grouping.

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CONDENSATIONS AT THE GAMMA POSITION OF BETA-KETOALDEHYDES. A NEW METHOD OF ANGULAR METHYLATION[1]

Sir:

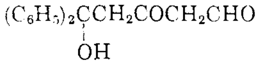
We wish to report that alkylations and other condensations have been directly effected at the gamma position of certain β-ketoaldehydes (hydroxymethylene ketones) through intermediate dianions. This is a novel mode of reaction of β-ketoaldehydes, although similar condensations at the terminal methyl group of acetylacetone and of other β-diketones previously have been accomplished through their dicarbanions.[2] The experimental procedure employed with β-diketones[2] was altered for β-ketoaldehydes, which are more reactive. The latter compounds were handled as their alkali metal salts or copper chelates.

Sodio formylacetone was prepared from acetone and ethyl formate in the usual manner[3] and added to a molecular equivalent of potassium amide in liquid ammonia. The resulting olive green dicarbanion I was treated with a molecular equivalent of benzyl chloride. After evaporation of the ammonia, alkylation product II was isolated in 80% yield as the copper chelate, m.p. 176–178°. This product was identified by comparison with an authentic sample of the chelate of II (lit. m.p. 176°) prepared by the method of Joshi, *et al.*[4]

$\bar{C}H_2CO\bar{C}HCHO$
I

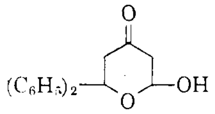
$C_6H_5CH_2CH_2COCH_2CHO$
II

Similarly, dicarbanion I was condensed with benzophenone to give hydroxy-β-ketoaldehyde III, which was isolated as its copper chelate (blue needles), m.p. 177–178°, in 67% yield. *Anal.* Calcd. for $C_{34}H_{30}O_6Cu$: C, 68.27; H, 5.06; Cu, 10.62. Found: C, 68.17; H, 5.10; Cu, 10.79. Treatment of this chelate with acid afforded a white crystalline product, m.p. 123–124°, infrared peaks (KBr): 2.98 μ (OH), 5.85 μ (non-conjugated ketone). *Anal.* Calcd. for $C_{17}H_{16}O_3$: C, 76.10; H, 6.01. Found: C, 76.00; H, 6.00. The product failed to give a positive enol test with ethanolic ferric chloride. It is tentatively assigned the hemiacetal structure IV.



$(C_6H_5)_2\underset{\displaystyle OH}{\underset{|}{C}}CH_2COCH_2CHO$

III



IV

Interestingly, the present method of alkylation furnished a new procedure for introducing an angular methyl group into 1-decalone at the 9-position. Sodio 2-formyl-1-decalone (V) was prepared in the usual manner[5] and added to a molecular equivalent of potassium amide in liquid ammonia. The resulting dicarbanion was treated with methyl iodide to give a mixture of the isomers of VII, which was isolated in about 60% yield as the copper chelate, m.p. 171–175°. After two recrystallizations from ethanol the chelate melted 183–185°. *Anal.* Calcd. for $C_{24}H_{34}O_4Cu$: C, 64.05; H, 7.61; Cu, 14.12. Found: C, 63.85; H, 7.45; Cu, 13.88. Treatment of the crude chelate with acid and removal of the formyl group by alkali, afforded 9-methyl-1-decalone (VIII) in 85% yield. Vapor phase chromatography on a Ucon Polar column indicated that VIII was a 56:44 mixture of the *trans* and *cis* isomers. The isomers also were separated and identified by their relative rates of semicarbazone formation, *trans* isomer m.p. 218.5–219° (lit. m.p. 219–220°) *cis* isomer m.p. 225–226° (lit. m.p. 226–227°).[6]

This direct method of introducing an angular methyl group appears more convenient than those involving the intermediate preparation from V of

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[1] Supported by the National Science Foundation (NSF-G14527).

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