and 4.02 (m, 3); ir 1685, 1626, 1200, and 1160 cm^{-1}; uv max (MeOH) 250 nm (ε 34,000).

Anal. Calcd for $C_{15}H_{21}NO_3$: C, 68.42; H, 8.04; N, 5.32. Found: C, 68.59; H, 8.07; N, 5.31.

Tritiglamide (9).—A solution of 2.57 g (0.02 mol) of tiglyl chloride, bp 63-66° (10 mm), and 1.0 g (0.01 mol) of tiglamide, mp 76–78°, in 40 ml of methylene chloride was cooled to −20°. A 1.6-ml sample (0.02 mol) of pyridine was added slowly with shaking and the resulting homogeneous solution was warmed to −5° over a 12-hr period and then allowed to remain at room temperature for 1 day. Processing this solution in the customary manner afforded 1.8 g of a crude, liquid product. Crystallization from cyclohexane produced 300 mg of a solid which melted over a wide range. A thin layer chromatogram, developed with 2% methanol in chloroform, revealed that the solid consisted of two components (R_f 0.3 and 0.6 on silica gel GF-254). Column chromatography employing 20 g of 100 mesh activated silica gel eluted with 200 ml of chloroform afforded first 166 mg of **9** exhibiting only a single spot on tlc and showing physical properties as follows: mp 80–83°; nmr τ 8.2 (m, 18) and 3.5 (m, 3); ir 1700, 1660, and 1250 cm^{-1}.

Anal. Calcd for $C_{15}H_{21}NO_3$: C, 68.42; H, 8.04; N, 5.32. Found: C, 68.44; H, 8.10; N, 5.21.

The second compound eluted appeared to be ditiglamide: mp 88–94°; ir 3510, 1750, 1710, 1680, and 1650 cm^{-1}; nmr τ 8.2 (m, 12), 3.5 (m, 2), and 1.5 (s, 1, NH).

Tri(1-cyclopentene-1-carbonyl)amide (10).—1-Cyclopentene-1-carboxylic acid was prepared from cyclopentanone by the method of Cook and Linstead[11] and converted with thionyl chloride into 1-cyclopentenylcarboxylyl chloride, bp 57° (13 mm). To 5.22 g (0.040 mol) of the acid chloride in 50 ml of methylene chloride cooled to −35° was added from a syringe 3.5 ml (0.043 mol) of anhydrous pyridine. Immediately 2.22 g (0.02 mol) of 1-cyclopentene-1-carboxamide, mp 210° subl, was stirred into the solution. After 30 min at −35° a white solid formed which prevented effective stirring. The heterogeneous mixture was warmed to 10° during a 20-hr period. During this time most of the solid present at −35° had dissolved and did not reprecipitate on cooling to −35°. The mixture again was warmed to room temperature and was processed in the customary manner. In this way was obtained 5.0 g of crude crystals, which by comparative spectra contained 19% anhydride: nmr 7.94 (m, 6), 7.38 (m, 12), and 3.03 (t, 3); ir 1730 and 1780 cm^{-1}. Two recrystallizations of crude solid from cyclohexane afforded 3.5 g of analytically pure **10**: mp 126–131°; nmr τ 8.00 (m, 6), 7.45 (m, 12), and 3.39 (m, 3); ir 1748, 1710, 1692, and 1640 cm^{-1}; uv max (MeOH) 239 mμ (ε 28,000); mass spectrum *m/e* 299 (M^+) and 95 (100).

Anal. Calcd for $C_{18}H_{21}NO_3$: C, 72.22; H, 7.07; N, 4.68. Found: C, 72.09; H, 7.20; N, 4.62.

Tri(1-cyclohexene-1-carbonyl)amide (11).—Cyclohexene-1-carboxylic acid, mp 30°, was prepared from cyclohexanone *via* the intermediate cyanohydrin by a procedure analogous to that reported by Cook and Linstead[9] for the synthesis of cyclopentene-1-carboxylic acid.

A 28.8-g sample (0.20 mol) of cyclohexene-1-carboxylyl chloride, bp 95° (17 mm), in 200 ml of methylene chloride was cooled to −40°. An 18-ml portion (0.22 mol) of pyridine was added with vigorous stirring over a period of 5 min. Immediately 12.5 g (0.10 mol) of cyclohexene-1-carboxamide, mp 130–133°, was added and the heterogeneous mixture was then warmed to 12° during the next 20 hr. Work-up in the customary manner gave 33 g of off-white crystals, mp 100–110°. Recrystallization once from hexane–cyclohexane gave 29 g, mp 112–120°. Analytically pure material was obtained by column chromatography of a 5.0-g sample.

The column (90 g of 100 mesh activated silica gel) was eluted with benzene and then 3% anhydrous ethyl acetate in benzene to give 2.4 g of **11**: mp 119–121°; nmr τ 8.37 (m, 12), 7.75 (m, 3), and 3.35 (m, 3); ir 1730, 1680, 1670, and 1220 cm^{-1}; uv max (EtOH) 236 nm (ε 21,000); mass spectrum *m/e* 341 (M^+) and 109 (100).

Anal. Calcd for $C_{21}H_{27}NO_3$: C, 73.90; H, 7.87; N, 4.10. Found: C, 73.62; H, 8.04; N, 3.85.

Registry No.—**1**, 641-06-5; **2**, 22950-76-1; **3**, 22950-77-2; **6**, 22950-79-4; **7**, 22950-80-7; **8**, 22950-81-8; **9**, 22950-90-9; **10**, 22950-82-9; **11**, 22950-83-0; diisobutyramide, 3668-74-4; ditiglamide, 22950-91-0;

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[9] A. H. Cook and R. P. Linstead, *J. Chem. Soc.*, 956 (1934).

Bistriphenylsilyl Chromate. Oxidation of Olefins and Use in Ethylene Polymerization

L. M. Baker and W. L. Carrick

Research and Development Department, Union Carbide Corporation, Chemicals and Plastics, Bound Brook, New Jersey 08805

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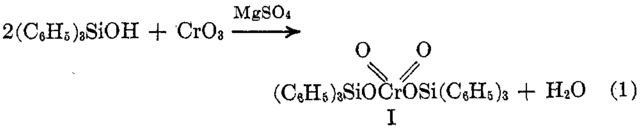
Bistriphenylsilyl chromate oxidatively cleaves olefins, giving the corresponding aldehydes and ketones along with reduced organochromium species. The reaction appears to be concerted. The silyl chromate also polymerizes ethylene at high pressure without any added cocatalysts. The active polymerization initiator is believed to be a low-valence organochromium compound.

There is increasing interest in highly specific reactions of organic derivatives of transition metals. Illustrative are olefin polymerization,[1] hydrogenation,[2] oxidation,[3] hydroformylation,[4] etc. Generally, these reactions involve a low-valence compound of the metal, and this fact stimulated the present interest in the mechanism of oxidation–reduction interactions of organic derivatives of transition metals.

Bistriphenylsilyl chromate[5] is a red crystalline solid, containing hexavalent chromium. It is easily prepared from triphenylsilanol and chromium trioxide. It is a



$$2(C_6H_5)_3SiOH + CrO_3 \xrightarrow{MgSO_4} (C_6H_5)_3SiO\overset{O\ \ O}{\overset{\diagdown\ \diagup}{Cr}}OSi(C_6H_5)_3 + H_2O \quad (1)$$

I

powerful oxidizing agent which enters into a number of complex reactions.

Results and Discussion

Treatment of a heptane or carbon tetrachloride solution of bistriphenylsilyl chromate with pentene-1,

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[1] K. Ziegler, E. Holzkamp, H. Breil, and H. Martin, *Angew. Chem.*, **67**, 541 (1955).

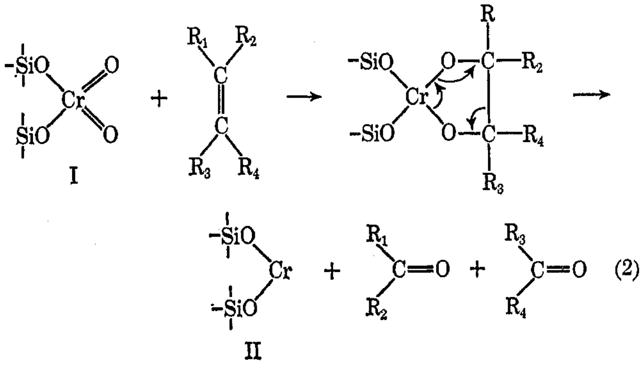
[2] J. Halpern, J. F. Harrod, and B. R. James, *J. Amer. Chem. Soc.*, **83**, 753 (1961).

[3] J. Smidt, W. Hofner, R. Jirn, J. Sedlemeier, R. Sieber, R. Ruttinger, and H. Kojer, *Angew. Chem.*, **71**, 176 (1959); (b) L. M. Baker and W. L. Carrick, *J. Org. Chem.*, **33**, 616 (1968).

[4] R. F. Heck and D. S. Breslow, *J. Amer. Chem. Soc.*, **83**, 4023 (1961).

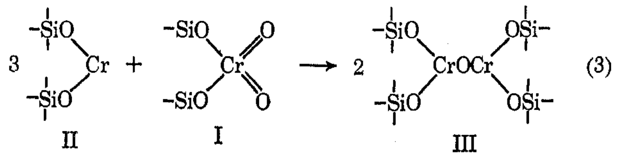
[5] F. E. Granchelli and G. B. Walker, Jr., U. S. Patent 2,863,891 (1958).

cyclopentene, cyclohexene, hexene-1, heptene-1, octene-2, styrene, acenaphthene, or *trans*-stilbene caused reduction of the chromium with formation of a green precipitate. Removal of the latter by filtration and investigation of the filtrates by infrared spectroscopy revealed the presence of carbonyl absorption in every case. A carbon tetrachloride solution containing equimolar amounts of styrene and bistriphenylsilyl chromate (I) was heated at reflux for 24 hr, and the resulting green precipitate was removed by filtration. The filtrate contained benzaldehyde and formaldehyde. Analogous experiments with *trans*-stilbene gave only benzaldehyde. No benzoic acid was detected, although oxidation of benzaldehyde to benzoic acid by numerous oxidizing agents readily occurs under mild conditions. Oxidation of benzaldehyde to benzoic acid should be easier than oxidation of stilbene to benzaldehyde. However, the fact that this second step does not occur argues that the primary olefin oxidation proceeds by a specific and unique mechanism,[3b] such as that shown.



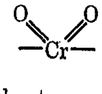
(2)

The divalent chromium ester II probably reacts with unconverted I to give the more stable trivalent species. Air oxidation could also convert II into III.



(3)

The green solid from the initial oxidation should be reduced chromium ester II or III. Infrared spectra of the green precipitates were identical regardless of the olefin used for reduction, and showed absorptions due to the $(C_6H_5)_3SiO$ group. The chief difference between these spectra and that of the original chromate ester I was the absence of absorptions at 10.1 and 10.3 μ due to the chromate group



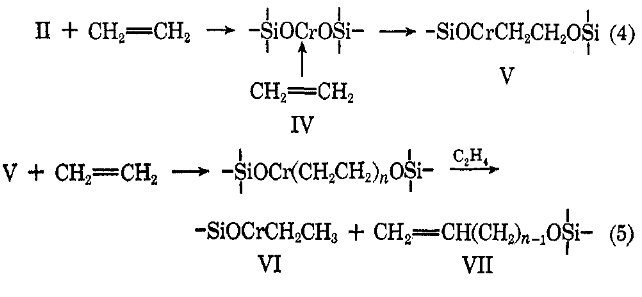
Attempts were made to prepare compound II by reaction of sodium triphenylsilanolate with chromous chloride in tetrahydrofuran. Treatment of the reaction mixture with pentane afforded a light bluish green precipitate which became dark green during isolation, even under a nitrogen atmosphere. The infrared spectrum was identical with that of the green solids from the olefin oxidations. Hydrolysis of the light green product in water afforded a mixture of triphenylsilanol and chromic oxide. Therefore, it appears that sodium triphenylsilanolate reacts with chromous chloride to give II, which is easily oxidized by oxygen or is hydrolytically decomposed to III, and that the final product is the same as the green solid from the olefin oxidation.

Low-valence transition metal compounds are the active sites in many polymerization catalysts.[6,7] Since the chromate ester I is reduced by olefins its polymerization activity was tested. Treatment of a cyclohexane solution of the chromate ester with ethylene without added cocatalyst caused rapid polymerization at elevated temperatures and pressures, as shown in Table I. Addition of an aluminum alkyl to the system at room temperature and atmospheric pressure also caused reduction of the chromium with the immediate onset of polymerization of ethylene. Oxygen was excluded to minimize free-radical polymerization. In a control experiment, ethylene was treated with benzoyl peroxide in cyclohexane at 21,000 psig and 125° and the only product was a small quantity of low molecular weight oil, which is the expected product of a radical polymerization under these conditions. This fact and the high density of the polymer obtained from chromate ester catalysis shows that the transition metal species is critical in the latter case.

TABLE I
ETHYLENE POLYMERIZATION WITH CHROMATE ESTER

$[(C_6H_5)_3SiO]_2CrO_2$, g	Temp, °C	Ethylene pressure, psi	Polymer yield, g	Melt index	Density
5.0	130	21000	170	0.002	0.956
1.0	150	20000	55	0.04	0.950
2.0	150	5000	20	0.2	0.948
0.5	175	20000	55	4.3	0.944

Previous work on transition metal polymerization catalysts supports a propagation mechanism involving coordination of the monomer to the transition metal, followed by rearrangement.[6,7]



$$\text{II} + CH_2{=}CH_2 \rightarrow \underset{\substack{\uparrow \\ CH_2{=}CH_2 \\ \text{IV}}}{-\overset{|}{\underset{|}{Si}}OCrO\overset{|}{\underset{|}{Si}}-} \rightarrow \underset{\text{V}}{-SiOCrCH_2CH_2O\overset{|}{\underset{|}{Si}}} \quad (4)$$

$$\text{V} + CH_2{=}CH_2 \rightarrow -\overset{|}{\underset{|}{Si}}OCr(CH_2CH_2)_nO\overset{|}{\underset{|}{Si}}- \xrightarrow{C_2H_4} \underset{\text{VI}}{-SiOCrCH_2CH_3} + \underset{\text{VII}}{CH_2{=}CH(CH_2)_{n-1}O\overset{|}{\underset{|}{Si}}-} \quad (5)$$

In the present case, this mechanism predicts ultimate formation of a low-valence chromium alkyl VI and a polymer molecule terminated in a triphenylsiloxy group VII. Polyethylene prepared by chromate ester catalysis was green in color Cr^{III} and showed infrared absorptions characteristic of the triphenylsiloxy group. The latter could be removed only by hydrolysis of the polymer with dilute acid, followed by solution of the polymer in xylene and reprecipitation in alcohol. This supports the sequence shown as eq 4 and 5.

In conclusion, it was shown that bistriphenylsilyl chromate oxidatively cleaves olefins, the reaction forms

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[6] D. B. Ludlum, A. W. Anderson, and C. E. Ashby, *J. Amer. Chem. Soc.*, **80**, 1380 (1958).

[7] F. J. Karol and W. L. Carrick, *ibid.*, **83**, 2654 (1961).

an active catalyst for ethylene polymerization, and a mechanism relating these facts to previous work is proposed.

Experimental Section

Bistriphenylsilyl Chromate.—A mixture of 15 g (0.054 mol) of triphenylsilanol, 15 g (0.15 mol) of chromium trioxide, and 5.0 g of anhydrous magnesium sulfate in 450 ml of carbon tetrachloride was shaken for 24 hr at room temperature in a light-tight flask. The red-orange mixture was filtered to remove solids and the product was recovered from the carbon tetrachloride solution by evaporation. Recrystallization of the dark residue from hot heptane gave orange needles of bistriphenylsilyl chromate: mp 153–155°; yield 10.1 g (60%). *Anal.* Calcd for $C_{36}H_{30}Si_2CrO_4$: C, 68.12; H, 4.76; Cr, 8.19. Found: C, 68.52; H, 4.97; Cr, 8.15%. The infrared spectrum showed strong absorptions at 10.15 and 10.27 due to Cr–O stretching vibrations.

Ethylene Polymerization with Bistriphenylsilyl Chromate.—In a typical example, 100 ml of cyclohexane, which had been previously dried by purging with nitrogen, was charged into a dry and nitrogen-filled 300-ml stirred autoclave. To this was added 0.5 g of bistriphenylsilyl chromate and the mixture was purged with nitrogen for several minutes before sealing the autoclave. The vessel was heated to 170° and pressure-bled several times to remove nitrogen. Ethylene was charged to an initial pressure of 20,000 psi, and the reaction was allowed to proceed for 4 hr. Temperature within the vessel was maintained at 170–175°. Approximately 20 g of a solid polyethylene was obtained, melt index 4.3.

Reaction of Bistriphenylsilyl Chromate with Olefins.—In a typical experiment, 3.20 g of bistriphenylsilyl chromate (5.05 mmol) dissolved in 5 ml of carbon tetrachloride was added to 1.06 g (12.9 mmol) of cyclohexene in a sealed tube. After agitation in a wrist-action shaker for 5 days, the sample was removed and centrifuged in a polypropylene tube at 14,000 rpm. The supernatant liquid showed the presence of triphenylsilanol as well as carbonyl. The green solid was extracted with moist ether for 48 hr, after which period 1.32 g of triphenylsilanol, mp 152–154°, was removed from the ether extract. This material was identified by means of its infrared spectrum as well as a mixture melting point with an authentic sample of triphenylsilanol, 151–154°. The infrared spectrum of the green residue at this point still exhibited absorptions characteristic of the triphenylsiloxy group. The green precipitate was then heated under reflux in dilute aqueous sulfuric acid for 24 hr and again extracted with wet ether. Upon drying, the green residue weighed 1.03 g. No further extraction was attempted, although the infrared spectrum of the latter material still exhibited the presence of the triphenylsiloxy group.

The infrared spectrum of the green residue [tetrakistriphenylsiloxydichromium(III) oxide] prior to extraction exhibited strong absorptions at 3.0, 3.3, 6.3, 6.74, 7.02, 7.52, 7.70, 7.95, 8.45, 8.98, 9.08, 9.40, 9.63, 9.72, 10.03, 10.7–11.8 (very broad), 13.40, 13.55, 14.10, and 14.35 μ.

The same green residue as identified by infrared was obtained regardless of the olefin used. Analogous reactions to the above described were carried out using cyclopentene, hexene-1, heptene-1, ethylene, octene-2, styrene, acenaphthene, and pinene. For example, 1.0 g of bistriphenylsilyl chromate and 0.18 ml of styrene contained in carbon tetrachloride were heated gently for several hours. The resulting green precipitate was removed by filtration and analyzed. *Anal.* Calcd for $C_{72}H_{60}Si_4Cr_2O_5$: C, 70.79; H, 4.95; Cr, 8.52. Found: C, 70.70, 70.73; H, 5.02, 5.12; Cr, 7.3.

Upon removal of the green precipitate, a strong odor characteristic of benzaldehyde was observed. Infrared examination of the filtrate showed that every major band present in the benzaldehyde spectrum was observed in the spectrum of the filtrate. Reaction of a portion of the filtrate with 2,4-dinitrophenylhydrazone reagent afforded a yellow crystalline derivative, mp 234–237° (lit.[8] mp 237° for 2,4-DNP of benzaldehyde). A 2,4-DNP of an authentic sample of benzaldehyde was prepared and found to have mp 237–238°, with above derivative mmp 234–238°.

In a separate experiment, a sample of the filtrate when treated with chromotropic acid in sulfuric acid afforded a positive test for the presence of formaldehyde. Control experiments using styrene and benzaldehyde alone and mixed afforded a negative test wich chromotropic acid.

Preparation of Bistriphenylsiloxychromium (II).—Into a stirred slurry containing 2.4 g (0.1 mol) of sodium hydride in tetrahydrofuran was added dropwise a solution containing 27.6 g (0.1 mol) of triphenylsilanol in tetrahydrofuran. Upon completion of the addition, the solution was colorless. To this was added 6.15 g (0.05 mol) of chromous chloride, and the reaction mixture was heated under reflux for 36 hr. A finely divided precipitate was removed from the supernatant green solution by filtration and was found to give a neutral solution in water with a positive halide test. This precipitate was believed to be sodium chloride. The filtrate was poured into excess pentane, affording a light green precipitate (II?), which was collected. This material was initially soluble in water but soon deposited a finely divided white material which was identified as triphenylsilanol. The green aqueous solution, upon further standing, afforded a small amount of a dark green precipitate, probably Cr_2O_3. Compound II, upon standing for 3 days under nitrogen or for several minutes in air afforded a dark green amorphous solid, probably an oxidation product, which no longer exhibited solubility in water. The infrared spectrum of this material was nearly identical with that of the precipitate obtained from the reaction of bistriphenylsilyl chromate with olefins. It appears that the initially formed bistriphenylsiloxychromium (II) reacts with water to form triphenylsilanol and chromic oxide, and rapidly oxidizes to afford tetrakistriphenylsiloxydichromium (III) oxide.

Registry No.—I, 1624-02-8; II, 23025-54-9; III, 22979-12-0.

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[8] R. L. Shiner, A. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 4th ed, John Wiley & Sons, Inc., New York, N. Y., 1956, p 231.