1-Phenyl-3-methylhex-1-en-4-yne (40, entry 1): NMR (270 MHz) 7.3 (m, 5 H), 6.60 (d, J = 16 Hz, 1 H), 6.10 (dd, J = 16, 6 Hz, 1 H), 3.28 (m, 1 H), 1.86 (d, J = 2.0 Hz, 3 H), 1.31 (d, J = 6.5 Hz, 3 H).

1-Phenyl-3-butylhex-1-en-4-yne (40, entry 5): NMR (270 MHz) 7.2 (m, 5 H), 6.58 (br d, 16.0 Hz, 1 H), 6.11 (dd, J = 16.0, 7.0 Hz, 1 H), 3.15 (m, 1 H), 1.86 (d, J = 2.4 Hz, 3 H), 1.57 (m, 2 H), 1.30 (m, 4 H), 0.89 (t, J = 7 Hz, 3 H); MS (t_R = 9.4 min), m/e (relative intensity) 212 (6, M$^+$), 170 (46), 155 (47), 141 (17), 129 (14), 128 (18), 115 (21), 91 (100), 77 (21).

1-Phenyl-5-methylnona-1,3,4-triene (41, entry 5): NMR (270 MHz) 7.35–7.15 (m, 5 H); 6.57 (dd, J = 16.0, 9.4 Hz, 1 H), 6.43 (d, J = 16.0 Hz, 1 H), 5.89 (dq, J = 11.9, 2.7 Hz, 1 H), 2.01 (tm, J = 8 Hz, 2 H), 1.75 (d, J = 2.7 Hz, 3 H), 1.39 (m, 4 H), 0.91 (t, J = 7.4 Hz, 3 H); IR (methylene chloride) 3070, 3030, 3005, 2950, 2920, 2860, 2845, 1935, 1620, 1590, 1490, 1440, 1360, 1260; MS (t_R = 7.5 min), m/e (relative intensity) 212 (23, M$^+$), 169 (5), 156 (14), 155 (100), 154 (15), 153 (22), 141 (9), 129 (15), 128 (14), 115 (29), 91 (27), 77 (20).

1,3-Diphenylpenta-1,3,4-triene (42): NMR (80 MHz) 7.3 (m, 10 H), 6.07 (d, J = 16.2 Hz, 1 H), 5.63 (d, J = 16.3 Hz, 1 H), 4.86 (d, J = 6.5 Hz, 1 H), 4.44 (d, J = 6.0 Hz, 1 H); IR (chloroform) 3070 (sh), 3050, 3020, 2920 (w), 2345, 1940 (br w), 1800 (br w), 1720 (br w), 1590, 1490, 1450, 1440, 1077, 1070, 1030, 910 (br).

Acknowledgment. We thank the U.S.–Israel Binational Science Foundation and the Israel Academy of Sciences and Humanities for their generous support of our program.

Registry No. 1, 58879-44-0; **2**, 51801-01-5; **3**, 103240-55-7; **4a**, 70677-93-9; **4b**, 103240-88-6; **5**, 103240-56-8; **6a**, 87639-27-8; **6b**, 103240-89-7; **7**, 103240-57-9; **7** (alcohol), 59277-57-5; **8**, 53544-89-1; **9**, 87802-86-6; **10**, 7614-93-9; 11, 103240-58-0; **12a**, 103240-59-1; **12b**, 103240-90-0; **13a**, 103240-60-4; **13b**, 103240-91-1; **14**, 93247-38-2; **15**, 103240-61-5; **16**, 103240-62-6; **17**, 103240-63-7; **18**, 103240-64-8; **19**, 4544-27-8; **20**, 103240-65-9; **21**, 103240-66-0; **22**, 103240-67-1; **23**, 103240-68-2; **24**, 103240-69-3; **25**, 103240-70-6; **26**, 103240-71-7; **27**, 103240-72-8; **28a**, 103240-73-9; **29a**, 103240-74-0; (*E*)-**29b**, 103240-75-1; (*Z*)-**29b**, 103241-01-6; **31**, 103240-76-2; **32**, 103240-77-3; **33**, 103240-78-4; **34**, 103240-79-5; **35**, 103240-80-8; (*E*)-**36a**, 103240-81-9; (*Z*)-**36a**, 103241-02-7; (*E*)-**36b**, 87639-29-0; (*Z*)-**36b**, 87639-30-3; **36c**, 87639-30-3; (*E*)-**37a**, 103240-82-0; (*Z*)-**37a**, 103240-95-5; **37b**, 103240-94-4; (*E*)-**38a**, 103240-83-1; (*Z*)-**38a**, 103240-97-7; **38b**, 103240-96-6; **39** (R = R′ = Me), 103240-84-2; **39** (R = Ph, R′ = Me), 103240-98-8; **39** (R = Me, R′ = Bu), 103240-99-9; **40** (R = R′ = Me), 103240-85-3; **40** (R = Me, R′ = Bu), 103241-00-5; **41** (R = Me, R′ = Bu), 103240-86-4; **42**, 103240-87-5; $H_2C{=}C{=}CH_2$, 463-49-0; PhCHO, 100-52-7; MeCH=CHCHO, 4170-30-3; $PhCH_2CH_2CHO$, 104-53-0; 4-$OHCC_6H_4CHO$, 623-27-8; $PhCH_2{=}CH_2CHO$, 104-55-2; PhC≡CH, 536-74-3; $BrC_6H_4CH{=}CH_2$, 1335-06-4; $HC{\equiv}CCH_2OH$, 107-19-7; $Ph(CH_2)_4CH(Me)CH_2Me$, 103240-92-2; $Ph(CH_2)_4CH(Me)(CH_2)_2Me$, 100216-99-7; $Me(CH_2)_2CH(Ph)(CH_2)_4Me$, 65185-83-3.

Polymer-Supported Reagents. 4.[1] Oxidation of Alcohols by Complex Chromates, Soluble Models and Supported Species[2]

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In the presence of quaternary ammonium species, chromium trioxide gave complex chromate salts $X(CrO_3)_n^-Q^+$ which were soluble in methylene chloride. These new compounds could be used as such for the oxidation of several alcohols but better efficiency was found under solid–liquid phase-transfer catalysis. Some of these complex chromates were fixed onto pyridinium and quaternary ammonium resins to give reactive polymers which were convenient in the oxidation of alcohols. The loading of the resins was achieved by an original solid–liquid–solid transfer process using quaternary ammonium salts as catalysts.

An increasing number of polymeric reagents have been designed to provide interesting facilities in organic syntheses,[3,4] one of them being the easier separation of the products from the reaction mixture.

Most of these reagents are involved in a one-step process leading to a discrete chemical modification of a substrate in solution; as the excess of reagent and spent reagent remains on the polymer, the workup is greatly facilitated. By percolating a substrate through a series of different polymeric reagents, it is possible to follow a sequence of chemical modifications to obtain the desired molecule (cascade reactions).[5]

Oxidation of alcohols to the parent carbonyl compounds is achieved by a lot of reagents,[6] though the general problem cannot be considered as definitely settled, particularly when using Cr(VI) derivatives,[7] since the workup of the reaction mixture is sometimes complicated.

Chromium trioxide is the most widely used starting material to prepare Cr(VI) oxidizing reagents by com-

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[1] For previous papers, see: (a) Gelbard, G.; Colonna, S. *Synthesis* **1977**, 113. (b) Colonna, S.; Re, E.; Gelbard, G. *J. Chem. Soc., Perkin Trans. 1* **1979**, 2248. (c) Brunelet, T.; Gelbard, G. *Nouv. J. Chim.* **1983**, *7*, 483. (d) Brunelet, T.; Gelbard, G.; Guyot, A. *Polym. Bull.* **1985**, *5*, 145.

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[4] For reviews, see: (a) Akelah, A.; Sherrington, D. C. *Chem. Rev.* **1981**, *81*, 557; *Polymers* **1983**, *24*, 1369. (b) Gelbard, G. *Actual. Chim.* **1984**, 84.

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0022-3263/86/1951-4016$01.50/0

Figure 1. Neutral and acidic complexes of CrO_3 with nitrogen heterocycles.

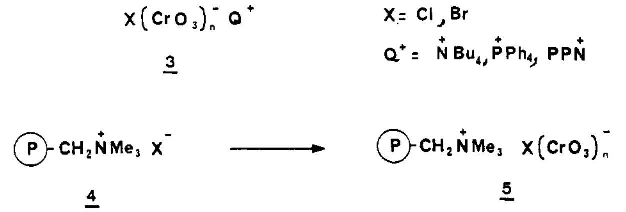

Figure 2. Soluble and polymer-supported onium complex chromates.

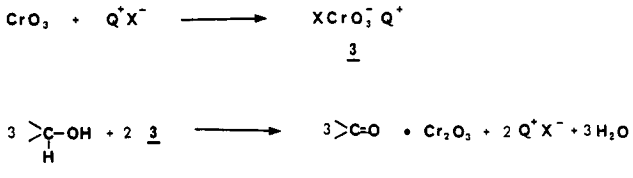

Figure 3. Preparation of onium chlorochromates and oxidation of alcohols.

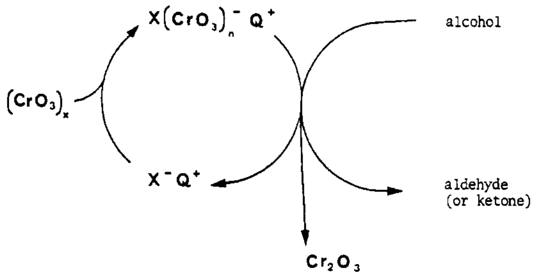

Figure 4. Oxidation of alcohols under solid–liquid phase-transfer catalysis.

Table I. Oxidation[a] of Octanols with Chromium Trioxide and Stoichiometric Amounts of Onium Salts

entry	alcohol	onium salt	yield,[b] % (time, min)
1	octan-1-ol	none	52 (5)[c]
2	octan-1-ol	$NBu_4^+Cl^-$	14 (5)
3	octan-1-ol	$NBu_4^+Br^-$	22 (5), 30 (60)
4	octan-1-ol	$PPh_4^+Cl^-$	8 (5)[d]
5	octan-2-ol	none	48 (5)[e]
6	octan-2-ol	$NBu_4^+Cl^-$	17 (5), 60 (60)
7	octan-2-ol	$NBu_4^+Br^-$	16 (5)
8	octan-2-ol	$NBu_4^+HSO_4^-$	70 (5)
9	octan-2-ol	$NBu_4^+CF_3SO_3^-$	80 (60)
10	octan-2-ol	$NBu_4^+p\text{-}CH_3C_6H_4SO_3^-$	70 (90)
11	octan-2-ol	$(C_{12}H_{25})_3N^+(CH_2)_3SO_3^-$[f]	60 (60)
	octan-2-ol	PCC **2**	80 (60)

[a] Standard procedure: alcohol (1 mmol), onium salt (1.5 mmol), chromium trioxide (1.5 mmol in 5 mL dry methylene chloride stirred at room temperature). [b] By GLC of octanal (entries 1–4) or octan-2-one (entries 5–11). [c] No remaining alcohol being detected due to over-oxidation to carboxylate. [d] Heterogeneous mixture, tetraphenylphosphonium chlorochromate precipitated partially as it formed. [e] 19% of remaining alcohol, oxidative cleavage of the ketone to carboxylates. [f] The betaines gave betaine chromates.

plexation with nitrogen heterocycles to give neutral complexes **1** with pyridine, dimethylpyrazole, acridine, and orthophenanthroline[9] and ionic complexes **2**, chlorochromates of pyridinium,[10] 2,2′-bipyridinium, 4-(dimethylamino)pyridinium,[11] pyrazinium *N*-oxide, and tripyridinium[12] (Figure 1).

Despite the claimed improvements brought by these reagents, they all suffer from the following drawbacks: (a) tedious recovery of the oxidation product from the precipitated or colloidal chromium(III) and/or -(IV) oxides; (b) the nitrogen heterocycle compound used as a coreagent is never recovered though it remains unaltered during the reaction.

Faced with these problems, we considered different approaches: (1) the use of other complex chromates, (2) the use of a coreagent in a catalytic way, (3) the use of reusable polymeric supported Cr(VI) reagents.

The last point afforded an additionally important feature concerning the safety on handling noxious reagents as they are bound to the resin; this had to be underlined as it has been shown that chromium is carcinogenic at *any stage of oxidation.*[13]

In the first part of this work,[1c] we described the preparation and the uses of polymer-supported neutral chromium(VI) complexes of general formula **1**. Here we report some new complex chromate salts **3** and their polymeric counterparts **5**; they differ from salts **2** by the following features: other complexing anions or betaines, neutral quaternary ammonium or phosphonium, and possible formation of complex polychromate anions.

Prior to the preparation of polymer-supported chromates **5** (obtained from anion exchange resins **4**) we undertook the study of the soluble species **3** (Figure 2).

Soluble Quaternary Ammonium Complex Chromates. We found the new family of compounds **3** very easy to prepare directly from chromium trioxide and quaternary ammonium salts; we reported first[14] the formation of tetrabutylammonium chlorochromate (**3**) (X = Cl, $n = 1$, $Q^+ = {}^+NBu_4$) simply by adding tetrabutylammonium chloride to a slurry of chromium trioxide in methylene chloride (Figure 3).

This method is, by far, more convenient than a recent one[15] and allowed us to prepare a series of compounds **3** [X = Cl, Br; $n = 1$; $Q^+ = {}^+NBu_4$, ${}^+P(C_6H_5)_4$, PPN^+[16]] which are described elsewhere.[17]

When stoichiometric amounts of chromic anhydride and quaternary ammonium salts were used, the soluble species formed exhibited oxidizing properties[18] related to the nature of the anion or the betaine used; octan-1-ol and octan-2-ol were chosen as significant substrates (Table I).

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(16) PPN^+ = bis(triphenylphosphino)immonium.

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(18) We found CrO_3 to be the only oxide giving soluble halo metallate when treated with tetrabutylammonium halides; attempts failed with CeO_2, CrO_2, CuO, Fe_3O_4, HgO, MnO_2, MoO_3, Pb_3O_4, and V_2O_5. We were able to prepare oxidizing chloro metallates $MCl^{m}{}_{n}{}^{+}$ $Q_m{}^{+}$ from $CuCl_2$, $FeCl_3$, and $HgCl_2$.[17]

Table II. Analytical and Preparative Scale Oxidation of Alcohols with CrO_3 and Catalytic Amounts of Onium Salts

entry	alcohol	onium salt	carbonyl	yield,[a] % (time, min)
12	octan-1-ol	$NBu_4^+Cl^-$	octanal	70 (5)
13	octan-1-ol	$NBu_4^+Cl^-$	octanal	60 (90)[b]
14	octan-2-ol	$NBu_4^+Br^-$	octan-2-one	99 (60)
15	octan-2-ol	$NBu_4^+CF_3SO_3^-$	octan-2-one	90 (45)
16	octan-2-ol	$NBu_4^+BF_4^-$	octan-2-one	90 (30)
17	octan-2-ol	$NBu_4^+F^-$	octan-2-one	99 (30)
18	octan-2-ol	$NBu_4^+HSO_4^-$	octan-2-one	99 (20)
19	octan-2-ol	$PPh_4^+Cl^-$	octan-2-one	99 (90)
20	octan-2-ol	$NBu_4^+ClCrO_3^-$	octan-2-one	95 (60)
21	cyclohexanol	$NBu_4^+Cl^-$	cyclohexanone	99 (20)
22	cyclohexanol	$NBu_4^+Cl^-$	cyclohexanone	70 (120)[b]
23	benzyl alcohol	$NBu_4^+Cl^-$	benzaldehyde	78 (20)[c]
24	benzyl alcohol	$NBu_4^+Cl^-$	benzaldehyde	63 (90)[b]
25	cinnamyl alcohol	$NBu_4^+Cl^-$	cinnamaldehyde	85 (15)[b]
26	menthol	$NBu_4^+Cl^-$	menthone	99 (20)
27	cyclohexen-2-ol	$NBu_4^+Cl^-$	cyclohexen-2-one	90 (24 h)
28	geraniol	$NBu_4^+Cl^-$	geranial	87 (24 h)[e]
29	nerol	$NBu_4^+Cl^-$	neral	95 (24 h)[f]

[a] By GLC. [b] Distillated product; preparative scale with 50 mmol of alcohol. [c] Together with 15% of benzoic acid. [d] By NMR. [e] Containing 27% of neral. [f] Containing 27% of geranial.

It has been reported that chromium trioxide was unreactive in an inert solvent;[19] we found (entries 1 and 5) that oxidation did occur but with a poor selectivity; most of the octanal formed is further oxidized to carboxylate and octan-2-one is cleaved to give chromium(III) carboxylates also. The IR spectra of solid residue of the reaction mixture exhibited in both cases bands at 1530 and 1440 cm^{-1} which are typical of $(RCO_2)_3Cr$; no free acid was detected (no band about 1715 cm^{-1}).

In all other cases, the selectivity was pretty good and the reactivity is in the same range as that of pyridinium chlorochromate (**2**) (entry 12); but here the reaction mixture is quite neutral. The acidic HSO_4^- anion (entry 8) afforded a shorter time for the reaction. Interestingly, anions with low coordinating power are able to form complexes with chromic anhydride (entries 9–11). Betaine salts (entries 11 and 12) should form betaine chromates.

A simple example of the oxidation reaction (Figure 3) showed that free onium halide is released from the complex chromate **3** after reduction to chromium(III) oxide,[20] so it could be reused to prepare fresh complex or, better still, used in a catalytic cycle (Figure 4). We succeeded in obtaining such a system: a small amount of onium salt in solution gave with solid chromium trioxide a small quantity of soluble complex chromate which oxidized the alcohol, and the onium salt was freed from the chromium(III) oxide which precipitated.

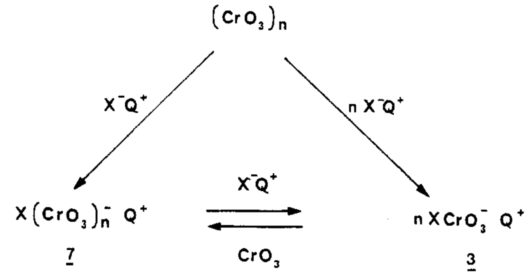

Figure 5. Formation of mono- and polycomplex chromates.

This solid–liquid phase-transfer catalytic system was checked on various alcohols (Table II) and was found to be *more efficient* than with stoichiometric amounts of onium chlorochromate (Table I) or pyridinium chlorochromate.[10] As reported above, anions with poor coordinating properties such as $CF_3SO_3^-$ (entry 15) or BF_4^- (entry 16) exhibited catalytic activity too. The best results were obtained with F^- (entry 17) and HSO_4^- (entry 18), the slight acidic feature of the latter appeared favorable.

This catalytic system required prolongated reaction time in the oxidation of allylic alcohols (entries 27–29) and some isomerization of the double bond occurred, but no epoxidation products were formed as it has been reported, using other Cr(VI) systems.[8a]

The striking fact that a *catalytic system ran at higher velocity* than a stoichiometric one raised the problem of the true nature of the oxidizing species operating in each case. In stoechiometric conditions, compounds **3** ($n = 1$) are orange-yellow in methylene chloride solution, whereas in PTC conditions the solution is dark-red. A blank experiment was run in the absence of alcohol using a molar ratio of $N^+Bu_4Cl^-/CrO_3$, 1/10; the supernatant solution was evaporated to dryness and gave a red-brown amorphous solid. The elemental analysis for the atomic ratio Cl/N/Cr gave 1/1/4, which corresponded to the formation of a tetrabutylammonium chloro*tetra*chromate **7** ($n = 4$).

According to the polymeric structure of solid chromic anhydride,[23,24] the effect of anions is to split the chain into small polychromate fragments **7** (Figure 5); similar reactions occurred when dissolving the chromic anhydride in water;[5a] the $HCrO_4^-$ and $Cr_2O_7^{2-}$ anions are the main species but the latter became preponderant at higher concentration and polychromates appeared.[25]

In the system described in Figure 5, complex chromates **3** and **7** can be interconverted by adding a suitable reagent: increasing the amount of onium salt Q^+X^- afforded the monochromate **3** and adding chromium trioxide to a solution of **3** gave again the polychromate **7**.[26]

The observed differences of reactivities between stoechiometric and catalytic conditions are then well explained by the difference of reactivities of complex monochromate $XCrO_3^-$ and complex polychromate $X(CrO_3)_n^-$ **7**, the latter being a better oxidizing species.

Some IR and UV data of these chromates are given in the supplementary material (see paragraph at the end of paper).

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(20) The oxidation level of the reduced chromium is still a matter of debate; though the formation of Cr(III) is generally accepted (ref 21 and 7b, p 204), H. C. Brown[22] concluded to the formation of Cr(IV), but caution was made by a referee of the paper. We attempted to bring conclusions by measuring the magnetism of the inorganic residue after the oxidation of isopropyl alcohol with an excess of Cr(VI) reagent. The occurrence of a mixture of Cr(VI) and Cr(III) could be established; the presence or the absence of a mixture of Cr(VI) and Cr(IV) could not be inferred owing to the size or the inorganic particles which did not allowed the ferromagnetism of Cr(IV) and the antiferromagnetism of Cr(III) to appear (unpublished results of the authors).

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(25) Freedman, H. L. *J. Am. Chem. Soc.* **1958**, *80*, 2072.

(26) It was beyond the scope of this work—directed toward polymeric oxidizing reagents—to study deeply these polychromates; solutions could contain chromates of various degree of condensation: the *n* value of isolated products might be a mean one.

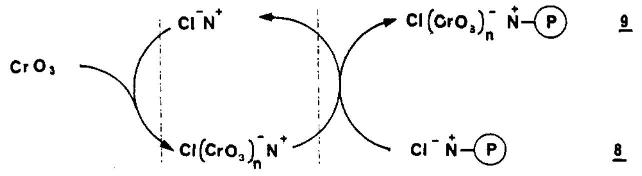

Figure 6. PTC process for the incorporation of complex polychromates into anion exchange resins (Cl^- can be replaced by others anions).

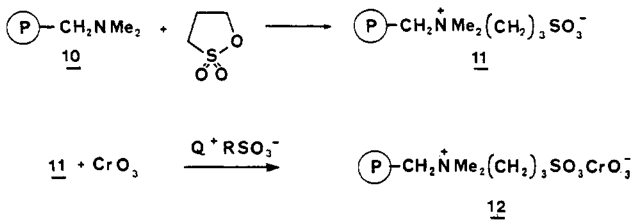

Figure 7. Preparation of sulfochromate betaine resins.

The solid–liquid phase-transfer catalytic (PTC) system described here is, by far, more convenient and faster than the liquid–liquid ones previously described;[27,28] the authors used there *stoechiometric* amounts of ammonium salt in water–solvent media and the acidity of the system led to oxidation of the ammonium salt.

Supported Quaternary Ammonium Complex Chromates. That study on soluble complex chromate enabled us to perform the incorporation of various chromates onto anion exchange resins and to recognize the oxidizing species in the polymer.

The supported reagents **5** were prepared from the corresponding anion exchange resins **8** (which are commercially available or easily obtained from chloromethylated polystyrene). Incorporation of complex chromates into the resins was achieved either by percolation of an aqueous acidic solution of chromic anhydride through a bed of resin in a column ("wet method") or by using a solution of tetrabutylammonium chloride in a triphase solid–liquid–solid system that we devised (PTC method) (Figure 6).

This new procedure is very convenient: the first step proceeded as in Figures 4 and 5 with the formation of small amounts of soluble ammonium chlorochromate **7** which then penetrated the resin wherein anion exchange occurred between the resident Cl^- and the incoming $Cl(CrO_3)_n^-$; the outcoming Cl^-, associated with $^+NBu_4$, reacted again with the solid chromic anhydride. The resin was finally washed with methylene chloride.

Similar procedures were used to prepare resin containing other complex chromates than chlorochromate by taking X^-Q^+ as a catalyst and an anion exchange resin in the required X^- form.

Supported betaine chromate resins **12** were prepared from (dimethylamino)methyl polystyrene resins **10** and propanesultone to give the betaine resins **11** which were afterward loaded according to the same PTC methods, as described above (Figure 7).

The data of supported chromium(VI) resins thus prepared are reported in Table III.

Table III. Supported Quaternary Ammonium Complex Chromates

entry	starting resin[a]	loading method	final resin	Cr/N[b]	capacity (mequiv Cr/g)
1	**8a**	PTC	**9a**	1.26	2.15
2	**8b**	PTC	**9b**	0.93	2.83
3	**8b**	PTC	**9b**	0.83	2.3
4	**8b**	wet	**9c**	0.83	2.3
5	**9b**	PTC	**9d**	2.05	4.23
6	**8e**	PTC	**9e**		
7	**8e**	wet	**9f**	0.5	2.4
8	**8g**	PTC	**9g**		
9	**8g**	wet	**9h**	0.49	2.5
10	**8i**	wet	**9i**	0.48	1.33
11	**8i**	PTC	**9j**	1.34	2.95
12	**11a**	PTC	**12a**		0.08
13	**11b**	PTC	**12b**		0.75

[a] The following resins are used: **8a**, gel type polystyrene containing 2% of DVB; **8b**, Amberlyst-A 26 macroporous polystyrene; **8e**, Amberlite IRA-958 macroporous polyacrylate; **8g**, Amberlite IRA-458 gel polyacrylate; **8i**, **8b** put in the $CF_3CO_2^-$ form; **11a**, sulfobetaine gel polystyrene; **11b**, sulfobetaine macroporous polystyrene. [b] Corresponds to the *n* value in formula **9**.

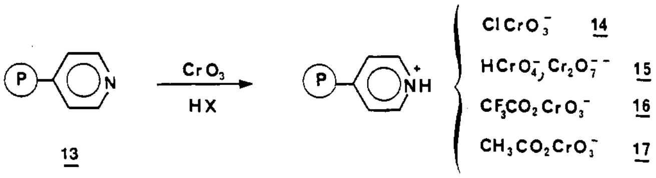

Figure 8. Preparation of supported acidic ammonium complex chromates.

The capacity, in terms of milliequivalents of chromium per gram of resin, was found to be strongly dependent on the nature of the resin, the loading, and the washing procedures. The wet procedure (entry 4) gave a resin the Cr/N ratio of which corresponded to the formation of chloromonochromate, whereas the PTC process (entry 5) gave a chlorodichromate. When this resin was washed with ethyl acetate instead of methylene chloride, the color of the washing indicated a leak of chromium trioxide and the Cr/N ratio of the final resins (entries 2 and 3) corresponded again to a chloromonochromate; Cr/N ratios of 1.26 (entry 1) and 2.05 (entry 5) were found in the resins. These lower values might be explained in several ways: (a) The specificity of the resin to exchange with the smaller complex anions which are present in the solution. (b) Better diffusion and a greater concentration of the smaller complex anions inside the resin. (c) An intraresin reaction between the resident Cl^- anions and the incoming polyanion $Cl(CrO_3)_n^-$,

$$Cl(CrO_3)_n{}^-N^+ + Cl^-N^+\text{-}\textcircled{P} \rightarrow$$

$$Cl(CrO_3)_{n/2}{}^-N^+ + Cl(CrO_3)_{n/2}{}^-N^+\text{-}\textcircled{P}$$

giving smaller units, the reaction being closely related to the transformation of compounds **7** to compounds **3** (Figure 5). The monochromate resins obtained either as above or by the wet process *could be reloaded to dichromate* by a PTC procedure similar to the one described in Figure 6. Anion exchange resins of macroporous (Table III, entry 6) or gel type (entry 8), both based on polyacrylate, were found reluctant to the PTC procedures; only partial loadings were obtained by the wet procedures (entries 7 and 9). It was not very clear why polyacrylate networks, which are more polar than polystyrene ones, were not proned to fix chromate moieties. On using trifluoroacetate as the complexing anion, the resin obtained by the wet procedure (entry 10) was half loaded with monochromate units; the PTC procedure gave a mixture of trifluoroacetato mono- and dichromate units (entry 11). Both gel **12a** and macroporous **12b** sulfobetaine resins gave low chromium contents (entries 12 and 13). Thus the macroporous polystyrene resin Amberlyst A-26® afforded

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Table IV. Supported Tertiary Pyridinium Complex Chromates

entry	starting resin[a]	final resin	mequiv Cr/g
1	**13a**	**14a**	1.20
2	**13a**	**14a**	1.04
3	**13b**	**14b**	3.01
4	**13a**	**15a**	1.94
5	**13b**	**15b**	2.37
6	**13a**	**16a**	1.37
7	**13a**	**17a**	1.60

[a] The following resins are used: **13a**, P 901 poly(vinyl)pyridine Ionac; **13b**, grafted poly(vinyl)pyridine on macroporous polystyrene.

the higher contents of chromium.

Supported Acidic Ammonium Complex Chromates. We described[1c] the use of poly(vinyl)pyridine resins **13** to prepare supported chromium trioxide complexes having a neutral structure similar to complex **1**. With the same resins we prepared supported ionic complexes with acidic characteristics (Figure 8). The incorporation of chromium(VI) anions was performed according to the "wet" procedure by suspending the basic polymer in a solution of chromium trioxide in water (resin **15**), in diluted hydrochloric acid (resin **14**) in diluted trifluoroacetic (resin **16**) or in acetic acid (resin **17**). The resins **14** and **15** were prepared independently from the similar ones published earlier.[29,30]

The chromium content of these acidic resins is reported in Table IV. The polyvinylpyridine chlorochromate (entry 1) is essentially a chloro monochromate as indicated by the Cl/Cr ratio. It was essential to wash the resin with acetone (or acetonitrile) to keep the integrity of the complex chromate; if the resin is washed with water (entry 2) as described in the literature[29] extensive hydrolysis occurs and the final product contains quite exclusively chromate $HCrO_4^-$ and dichromate $Cr_2O_7^{2-}$ units.[31] The procedure described here led to the true polyvinylpyridine chlorochromate. Chromate resins **15** (entries 3 and 4) were examined by IR spectroscopy in order to determine the nature of the chromate units which have been fixed; the observed bands at 938, 895, 878, and 768 cm^{-1} were compared to those given by potassium chromate K_2CrO_4 (955, 940, 905, 885, 840, 800, 765 cm^{-1}) and by pyridinium dichromate, $(C_5H_5NH)_2Cr_2O_7$ (940, 900, 885, 770 cm^{-1}). The presence of dichromate $Cr_2O_7^{2-}$ was then well established,[29] but the presence of chromate $HCrO_4^-$ cannot be ruled out. The set of the IR bands was not typical enough to draw clear-cut conclusions; furthermore, the pyridinium ring gave bands which interfered severely. The chromate anion $HCrO_4^-$ was claimed without any proof to be present on chromic acid anion exchange resins,[32] so the structure given to the commercially available chromium-supported resins should be severely questioned.

The capacity of these pyridinium resins—ranging between 1 and 3 mequiv Cr/g—was found somewhat lower than the one obtained by the aforementioned quaternary ammonium ones; here the macroporous poly(vinyl)pyridine resins **13b** (entries 3 and 5) gave a higher extent of chromium fixation.

Oxidation of Alcohols by the Chromium(VI)-Supported Resins. The oxidizing properties of neutral and acidic chromate resins described above were checked with typical primary and secondary alcohols; only resins with high chromium content were selected for experiments and it was decided to test the reactivity by short-timed reactions (4 h) so as to compare in each case the extent of the oxidation. To show the usefulness of these resins, some reactions were allowed to run up to completion.

The quaternary ammonium complex chromates were first examined in the oxidation of octan-1-ol, octan-2-ol, cyclohexanol, cyclohex-2-en-1-ol, menthol, and benzyl alcohol to their corresponding aldehyde or ketones. Moderate Cr/alcohol ratio were used and cyclohexane was chosen as solvent, though benzene exhibits better compatibility with polystyrene resins;[33] the results are given in Table V. Chlorochromate units on macroporous polystyrene afforded good yields of octanal (entry 2), octan-2-one (entry 4), cyclohexanone (entry 6), and menthone (entry 10). No significant differences appeared between the reactivity of chloro *mono-* (entry 5) and chloro *di-*chromate units (entry 7); the big differences observed above with soluble models were no longer found. This levelling effect which might be due to the polymer itself was noticed earlier.[1c] The polyacrylate resin did not seem very appropriate for such oxidations (entry 12). The efficiency of these quaternary ammonium chlorochromates was found to be similar to a previous acidic chromate one.[32] The best results were obtained with trifluoroacetatochromate resins which are believed to be very promising as they required short reaction times and moderate chromium/alcohol ratio (entries 15–19). Benzylic (entry 9) and allylic (entry 11) alcohols are poorly oxidized or require a large excess of reagent or prolongated reaction time; this inertness let out an interesting selectivity of the new complexes described here. When using the pyridinium chromate resins (see paragraph at the end of paper about supplementary material), the trifluoroacetatochromate anion (entries 17 and 19) exhibited the higher reactivity. The increasing order of reactivity of the complex chromate anions

$$HCrO_4^-,\ Cr_2O_7^{2-} < ClCrO_3^- < CF_3CO_2CrO_3^-$$

was found in both quaternary ammonium and pyridinium resins; this order followed the decreasing basicity of the complexing anion bound to chromium.

Conclusions

New complex chromate anions were found to be effective oxidants and easy to prepare by means of quaternary ammonium salts; the solid–liquid phase-transfer catalysis led to the formation of complex polychromates which were the species involved in the oxidation and in the incorporation of chromium into anion exchange resins. The supported quaternary ammonium complex chromates thus obtained exhibited effective oxidizing properties toward alcohols with a moderate excess of reagent vs. substrate. In our hands, acidic pyridinium resins were found to be less reactive than quaternary ammonium ones.

Thus many factors appeared to govern the efficiency of supported chromium(VI) species: Quaternary ammonium chromates are more reactive than tertiary pyridinium ones. These ionic salts are even more reactive than the neutral supported chromium trioxide complexes reported earlier by us.[1c,d] The reactivity of a complex chromate $XCrO_3^-$ increased as the basic feature of the complexing ion X^- decreases. Solvent effects modify the diffusion of substrates and products inside the resin; nonpolar solvents

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Table V. Oxidation of Alcohols with Supported Complex Chromates

entry		actual capacity	solvent	alcohol	Cr/alcohol ratio	t_H (θ°)	yield, %
	quaternary ammonium chlorochromate						
1	**9b**	2.3	cyclohexane	octan-1-ol	3.5/1	4 (70)	34
2	**9b**	2.3	cyclohexane	octan-1-ol	7/1	12 (70)	80
3	**9b**	2.3	cyclohexane	octan-2-ol	5.1/1	4 (70)	39
4	**9b**	2.3	cyclohexane	octan-2-ol	7/1	12 (70)	92
5	**9b**	2.3	cyclohexane	cyclohexanol	3.1/1	4 (70)	45
6	**9b**	2.3	cyclohexane	cyclohexanol	6/1	12 (70)	90
7	**9d**[a]	4.23	cyclohexane	cyclohexanol	5/1	4 (70)	50
8	**9a**	2.15	cyclohexane	cyclohexanol	6/1	12 (70)	5
9	**9b**	2.3	cyclohexane	benzyl alcohol	10/1	12 (70)	73[b]
10	**9b**	2.3	cyclohexane	menthol	9/1	12 (70)	98
11	**9b**	2.3	cyclohexane	cyclohex-2-en-1-ol	8/1	8 (70)	2
12	**9f**	2.4	cyclohexane	cyclohexanol	6/1	12 (70)	30
	quaternary ammonium trifluoroacetatochromate						
13	**9j**	1.33	acetone	octan-2-ol	8/1	4 (50)	8
14	**9j**	1.33	ethylacetate	octan-2-ol	10/1	10 (50)	90
15	**9j**	1.33	cyclohexane	octan-2-ol	7.6/1	4 (70)	90
16	**9j**	1.33	cyclohexane	octan-2-ol	3.8/1	4 (70)	82
	pyridinium trifluoroacetatochromate						
17	**16a**	1.37	acetone	octan-2-ol	25/1	4 (50)	96
18	**16a**	1.37	acetone	octan-2-ol	7.3/1	4 (50)	55
19	**16a**	1.37	cyclohexane	octan-2-ol	3.4/1	8 (70)	69

[a] Chlorodichromate ($ClCr_2O_6^-$) resin. [b] Benzoic acid detected only in the acid washings of the resin after reaction; no trace was present in solution.

(cyclohexane) afford a good compatibility with the polystyrene skeleton. Macroporous resins give better results than gel type ones even when the latter are well swollen; this is already noticed with supported neutral complexes.[1d]

Experimental Section

Quaternary ammonium and phosphonium salts are commercially available products and were used as such without further purification. Alcohols subjected to oxidation and their corresponding aldehydes or ketones were purified by distillation. Analytical grade solvents were kept dry on 4-Å molecular sieves. The chromium contents of the resins were determined by elemental analysis or by redox titration.[34] GLC analysis were performed in the presence of dodecane or tetradecane as internal standard on a Carlo-Erba Fractovap 2150 apparatus fitted with a FID and connected to a Spectraphysics integrator; a 2.5 m × 4 mm stainless steel column filled with Carbowax 20M 15% on Chromosorb Q was used throughout this study with N_2 as carrier gas. IR and UV spectra were recorded on a Perkin-Elmer 297 and a Beckmann D.U. 50 apparatus, respectively.

Benzyltrimethylammonium Trifluoroacetate. Trifluoroacetic acid (4.45 g, 4.68 mmol) is added dropwise to 20 mL of a 40% methanolic solution (3.9 mmol) of benzyltrimethylammonium hydroxide; stirring and external cooling are ensured during the addition. The solution is evaporated to dryness and the residue is dissolved in 50 mL of chloroform and evaporated again; this is repeated three times. The final hygroscopic solid is dried under vacuum; yield 9.63 g (94%). Anal. Calcd for $C_{12}H_{16}NO_2F_3$ (263.26): F, 21.65; N, 5.32. Found: F, 20.45; N, 5.38.

Tridodecylammonium 3-Propanesulfonate. Tridodecylamine (6 g, 11.5 mmol) and 12.2 g (10 mmol) of propanesultone in 10 mL of dry toluene are heated 3 h at 110 °C with protection against air moisture; after cooling in an ice bath, the cristalline precipitate is thoroughly washed with pentane and recrystallized from methanol/ethyl acetate: yield 4 g (62%); mp 167–168 °C. Anal. Calcd for $C_{39}H_{81}O_3S$ (644.12): N, 2.18; S, 4.98. Found: N, 2.17; S, 4.90.

Resin 8a. Chloromethylated polystyrene (Merrifield polymer Fluka 2% DVB) (10 g, 27 mequiv) is put in a 200 mL round-bottomed flask fitted with a reflux condenser and allowed to swell to 15 nm in 25 mL of dimethoxymethane; 50 mL of a 30% aqueous solution of trimethylamine are added and the mixture is heated at 40 °C for 2 h. The reflux condenser is replaced by a distilling column and the mixture is heated at 50 °C; the polymer is collected on a fritted funnel and thoroughly washed succesively with water (500 mL), 3% aqueous hydrochloric acid (200 mL), and water (200 mL). The resin is transferred into a Soxhlet extractor, refluxed with acetone for 2 h, and vacuum dried at 65 °C for 24 h. The nitrogen content (3.19%) indicates a capacity of 2.28 mequiv ammonium/g.

Resin 8b. The macroporous Amberlyst A-26 resin (Rohm and Haas) with a capacity of 4.4 mequiv ammonium/g is washed with acetone in a Soxhlet extractor and vacuum dried.

Resins 8c and 8d. The polyacrylate anion exchange resins Amberlite IRA 958 (**8c**) of macroporous type (2 mequiv/g) and IRA 458 (**8d**) of gel type (3.2 mequiv/g) (both from Rohm and Haas) are washed with acetone and dried as above.

Resin 11a. (Dimethylamino)methyl polystyrene resin **10a** (from Fluka) (3 g, 8.7 mmol) and 2.42 g (19.9 mmol) of propanesultone in 10 mL of dry toluene are heated at 100 °C for 8 h with gentle stirring; the reaction mixture is protected from the air moisture. The resin is transferred into a Soxhlet extractor, washed with refluxing methylene chloride, vacuum dried, and weighed (4.6 g): IR (KBr) for sulfonate anion 1220–1170 (br), 1030 cm^{-1} (s). The analytical data (N, 2.58, and S, 8.48) show a betaine content of 2 mequiv/g.

Resin 11b. The same procedure as for resin **11a** is carried out with 6 g (28.8 mequiv) of macroporous (dimethylamino)methyl polystyrene resin (Amberlyst A-21 from Rohm and Haas) and 5.5 g (45 mequiv) of propanesultone; the analytical data (N, 3.72; S, 9.25) show a betaine content of 2.8 mequiv/g.

Resin 13a. The gel type poly(vinyl)pyridine P 901 (from Ionac Chemicals) is washed with methanol in a Soxhlet extractor and vacuum dried; the capacity is 5.9 mequiv N/g.

Resin 13b. This macroporous poly(vinyl)pyridine resin is prepared by grafting vinylpyridine onto a macroporous polystyrene resin according to the procedure described by one of us.[35]

Resin 9a. Resin **8a** (5.2 g, 11.8 mequiv) is washed with 20 mL of methylene chloride and put in a stopped Erlenmeyer flask with 25 mL of methylene chloride; 278 mg (1 mmol) of tetramethylammonium chloride and 1.2 g (12 mmol) of chromium trioxide are added and the flask is gently shaken for 3 h. The dark-red resin is collected on a fritted funnel, washed with ethyl acetate until clear filtrate is obtained, and finally vacuum dried: IR (KBr) 940, 900, 770 cm^{-1}.

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Resin 9b. The same procedure as above is carried out with 10 g of resin **8b**, 1 mmol of ammonium salt, and 45 mmol of chromic anhydride in 50 mL of methylene chloride; an improved capacity of 2.83 mequiv Cr/g is found.

Resin 9d. This chloro dichromate resin is obtained as for **9b** but methylene chloride is used for the final washing. The same resin is obtained by treating again chloro monochromate resin **9b** with ammonium salt and chromic anhydride in methylene chloride and by washing it with the same solvent.

Resin 9j. Wet resin **8b** (70 mL, 70 mequiv) is put in a glass column and slowly percolated with 2 L of a 10% aqueous solution of sodium hydroxide; this procedure allows the complete conversion of the resin into the hydroxide form.[36] The resin is washed with 500 mL of water and then added by small fractions into 200 mL of a stirred aqueous solution of 1 N trifluoroacetic acid. The stirring is maintained for 1 h. The resin is transferred again into the glass column for final washings with water (up to the neutrality of eluents), ethanol (200 mL), acetone (200 mL), and methylene chloride (150 mL). Anal. Calcd: N, 4.59; F, 18.68. Found: N, 4.62; F, 18.63. This trifluoroacetate resin (10 g, 32 mmol) is shaken with 263 mg (1 mmol) of tetrabutylammonium trifluoroacetate and 6 g (60 mmol) of chromium trioxide in 300 mL of methylene chloride. The workup with ethyl acetate affords a dark-red resin with a capacity of 2.95 mequiv Cr/g.

Resins 12a and 12b. Resin **11a** (4.6 g, 92 mmol), 337 mg (1 mmol) of tetrabutylammonium methanesulfonate (Fluka), and 2 g (20 mmol) of chromium trioxide are shaken together in 30 mL of methylene chloride. No coloration of the resin results from the red solution and the final resin **12a** exhibits small amounts of chromium. Resin **11b** (10 g, 28 mmol) is treated as mentioned above for resin **11a**; the final resin **12b** shows a capacity of only 0.75 mequiv Cr/g: IR (KBr) 945, 895 cm^{-1}.

Resin 9c. Acetone-washed resin **8b** (20 mL, 20 mmol) is rinsed with water in a glass column and percolated with a solution of 15 g (150 mmol) of chromium trioxide in 200 mL of 6 N hydrochloric acid; the washing with 600 mL of acetonitrile and the vacuum drying afford 14 g of a dark-orange resin with a content of 2.3 mequiv Cr/g.

Resins 9f and 9h. Moist resin **8c** (20 mL) is shaken for 1 h in a solution of 2 g (20 mmol) of chromium trioxide in 100 mL of 6 N hydrochloric acid; the resin is collected on a fritted funnel washed with acetone and vacuum dried. The resin **9f** (12 g) has a capacity of 2.4 mequiv Cr/g. The same procedure with 20 mL of resin **8d** gives 11.5 g of resin **9h** with a capacity of 2.5 mequiv Cr/g.

Resin 14a. Chromic anhydride (4.5 g, 45 mmol) is dissolved with external cooling in 20 mL of water and 5 mL of concentrated hydrochloric acid is slowly added; 5 g (29.5 mequiv) of resin **13a** are added portionwise. The reaction mixture is allowed to stand for 30 min with occasionnal shaking. The brown-orange resin is filtered on a fritted glass, washed with *acetonitrile* (200 mL), and vacuum dried at 60 °C for 3 h (yield 7 g). If the resin is rinsed with water, as reported elsewhere[29] analytical data show extensive hydrolysis of chlorochromate into chromate anion.

Resin 14b. The same procedure as for resin **14a** is carried out with resin **13b**.

Resin 15a. Chromium trioxide (5 g, 50 mmol) is slowly added to a stirred suspension of 6 g (35 mequiv) of resin **13a** in 20 mL of water; the stirring is maintained for 20 min and the resin is washed with water until the filtrate becomes colorless. Vacuum drying affords a light-yellow resin.

Resin 15b. The same procedure as for resin **15a** is carried out with resin **13b**.

Resin 16a. Chromic anhydride (2 g, 20 mmol) is suspended in 100 mL of acetonitrile and 1.55 mL (20 mmol) of trifluoroacetic acid are carefully added. The resin **13a** (3 g, 17.8 mequiv) is added portionwise and the stirring is maintained for 1 h. The resin is filtered, washed with acetonitrile, and vacuum dried.

Resin 17a. The same procedure as for resin **16a** is carried out but this time using acetic acid.

Oxidation of Alcohols by Solid–Liquid PTC. A typical example of oxidation on a analytical scale is as follows: 1.5 mmol of chromium trioxide and 0.075 mmol (5%) of quaternary ammonium salt are suspended in 2 mL of dry methylene chloride; 1 mmol of alcohol in 1 mL of methylene chloride is added dropwise. The reaction is monitored by TLC. Scaling-up to 50 mmol is performed in the same way: the final reaction mixture is filtered through a Celite pad and evaporated and the residue is triturated with ether; evaporation and distillation give the pure carbonyl compound.

Oxidation of Alcohols with Polymer-Supported Chromates. The reactions are performed with 2 mmol of alcohol dissolved in 10 mL of solvent according to the experimental data given in Tables VII and VIII; the solution and the resin are transferred to a Soxhlet extractor and washed with refluxing methylene chloride. An aliquot of the internal standard is added and the solution is analyzed by GLC.

Regeneration of the Resins. To check the integrity of the polymer during oxidation, a sample of resin **9b** is recovered after use and washed with 1 N hydrochloric acid until the filtrate becomes colorless. The resin is rinsed with water up to neutrality and the exchange capacity, measured by the usual ways,[37] is found to be identical with that of a fresh sample of resin **8a** (1 mequiv Cl^-/mL wet resin). A sample of a pyridinium resin **14b**, recovered after use, is washed as above with hydrochloric acid, rinsed with water, and neutralized with 1 N sodium hydroxide solution. The sample is washed with water (up to neutrality) and methanol and finally vacuum dried. The nitrogen analysis (N(%) = 10.0) is identical with that of the starting resin **13b**. Thus the regenerated resins are suitable for further use but mechanical attrition brings a weight loss of about 2%.

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Registry No. $NBu_4^+F^-$, 429-41-4; $NBu_4^+HSO_4^-$, 32503-27-8; $NBu_4^+Cl^-$, 10017-37-5; $NBu_4^+Br^-$, 60469-70-7; $PPh_4^+Cl^-$, 2001-45-8; benzyltrimethylammonium trifluoroacetate, 86826-65-5; tridodecylammonium propanesulfonate, 103982-08-7; poly(vinyl)pyridine, 9003-47-8; cinamyl alcohol, 104-54-1; menthol, 1490-04-6; octan-2-one, 111-13-7; tridodecylamine, 102-87-4; propanesultone, 1120-71-4; Amberlyst A-26, 39339-85-0; Amberlite IRA 958, 79620-27-2; Amberlite IRA 458, 9084-78-0; Amberlyst A-21, 9049-93-8; chromium trioxide, 1333-82-0; octan-1-ol, 111-87-5; octan-2-ol, 123-96-6; cyclohexanol, 108-93-0; benzyl alcohol, 100-51-6; cyclohexen-2-ol, 822-67-3; geraniol, 106-24-1; nerol, 106-25-2; octanal, 124-13-0; cyclohexanone, 108-94-1; benzaldehyde, 100-52-7; cinnamaldehyde, 104-55-2; menthone, 126-81-8; cyclohexen-2-one, 930-68-7; geranial, 141-27-5; neral, 106-26-3.

Supplementary Material Available: IR and UV data of complex chromates and polychromates; full analytical data of supported complex chromates; scheme of the interchange between supported quaternary ammonium chloromonochromate and chloropolychromates (5 pages). Ordering information is given on any current masthead page.

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[36] Rohm and Haas; Technical Bulletin No. IE 92-65, 1967; U.S. Patent 2 999 821 quoted therein.

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