warm to room temperature and then was poured into saturated ammonium chloride solution. Usual workup followed by flash chromatography[20] (20% EtOAc–hexane) afforded aldehyde **6a** (136 mg): mp 152–153 °C (from methanol); IR 3335, 2720, 1720, 970 cm^{-1}; ^{1}H NMR δ 0.55 (3 H, s, 18-CH_3), 0.80 (3 H, s, 19-CH_3), 2.3 (3 H, m, 24-H and 28-CH_2), 3.3–3.8 (2 H, m, 3 H and OH, 5.17–5.45 (3 H, m, 7-H, 22-H and 23-H), 9.75 (1 H, m, CHO); mass spectrum, *m/e* (relative intensity) 426 (M^+, 8), 271 (M – side chain + 2H, 28), 135 (52), 81 (67), 55 (100).

Anal. Calcd for $C_{29}H_{46}O_2$: C, 81.69; H, 10.80. Found: C, 81.74; H, 11.00.

The same reaction on **5b** (250 mg) afforded **6b** (200 mg) mp 145–146 °C (from methanol); $[\alpha]^{20}{}_D$ 2.5°; IR 3335, 2720, 1720, 970 cm^{-1}; ^{1}H NMR δ 0.55 (3 H, s, 18-CH_3), 0.80 (3 H, s, 19-CH_3), 2.3 (3 H, m, 24-H and 28-CH_2), 3.3–3.8 (2 H, m, 3 H and OH), 5.17–5.45 (3 H, m, 7-H, 22-H, and 23-H), 9.75 (1 H, m, CHO); mass spectrum, *m/e* (relative intensity) 426 (M^+, 8), 271 (M – side chain + 2H, 27), 135 (52), 81 (68), 55 (100).

Anal. Calcd for $C_{29}H_{46}O_2$: C, 81.69; H, 10.80. Found: C, 81.73; H, 11.12.

(22*E*,24*S*)- and (22*E*,24*R*)-5α-Ergosta-7,22-dien-3β-ols (1a and 1b). Aldehyde **6a** (100 mg) was dissolved in degassed toluene (10 mL) and was refluxed under nitrogen in the presence of tris(triphenylphosphine)chlororodium (100 mg) for 3 h. The mixture was filtered through a pad of silica gel G–Celite and the solvent was removed under reduced pressure. The residue was crystallized from methanol to yield stellasterol (**1a:** 65 mg; mp 159–160 °C; $[\alpha]^{23}{}_D$ 18° (lit.[5,6] mp 159–160 °C, $[\alpha]^{20}{}_D$ 7.8°); IR 3400–3300, 970 cm^{-1}; ^{1}H NMR δ 0.54 (3 H, s, 18-CH_3), 0.80 (3 H, s, 19-CH_3), 5.14 (1 H, m, 7-H); mass spectrum, *m/e* (relative intensity) 398 (M^+, 28), 383 (M – CH_3, 13), 300 (M – (C(20)–C(22) fission + 1 H), 20), 271 (M – (side chain + 2), 100), 255 (M – (side chain + H_2O), 52), 229 (30), 213 (22); all chemicophysical characteristics are identical.

Anal. Calcd for $C_{28}H_{46}O$: C, 84.42; H, 11.56. Found: C, 84.42; H, 11.49.

Similar treatment of aldehyde **6b** gave **1b**: mp 174–175 °C; $[\alpha]^{23}{}_D$ –21°; identical with an authentic sample.[21]

Anal. Calcd for $C_{28}H_{46}O$: C, 84.42; H, 11.56. Found: C, 84.48, H, 11.40.

Acknowledgment. We thank the Italian Research Council (CNR) for support and Professor G. Galli, Institute of Pharmacology and Pharmacognosy of the University of Milan, for mass spectra.

Registry No. **1a**, 50364-22-2; **1b**, 2465-11-4; **2**, 23738-34-3; **3a**, 76282-34-3; **3b**, 76299-35-9; **4a**, 76282-35-4; **4b**, 76332-76-8; **4c**, 76282-36-5; **4d**, 76299-36-0; **5a**, 76282-37-6; **5b**, 76332-77-9; **6a**, 76282-38-7; **6b**, 76332-78-0; 3-methyl-1-butyne, 598-23-2.

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Poly(vinylpyridinium dichromate): An Inexpensive Recyclable Polymeric Reagent

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In connection with our studies on the preparation and applications of recyclable polymeric reagents[1] for use in simple one-step processes, we have described recently a polymeric analogue[2] of pyridinium chlorochromate which was an effective reagent in the oxidation of alcohols into the corresponding aldehydes and ketones. The main advantage associated with the use of a polymeric reagent is the ease of purification of the final product since both the initial polymer, which may be used in excess to help drive the reaction to completion, and its byproduct are insoluble and can be separated by simple filtrations. Although our poly(vinylpyridinium chlorochromate),[2] PVPCC, met these objectives, not all of the reactive sites of the polymer were directly accessible and thus the amount of polymer which was required to carry out an oxidation reaction was larger than stoichiometric. Typically, the original PVPCC prepared from a commercially available cross-linked poly(vinylpyridine)[3] was best used in two- to fivefold excess, while another polymer-bound chromate reagent[4] based on a commercial Amberlyst A-26 resin was generally used in even larger excess.

Table I. Reaction of Poly(vinylpyridinium dichromate) with Benzyl Alcohol: Influence of Water, Trifluoroacetic Acid, and Solvent

reaction conditions[a]	solvent	% conversion[b] 15 min	70 min	2 h	18 h
PVPDC, wet	cyclohexane	75	92	96	>99
PVPDC, dried	cyclohexane	4	5	5	8
PVPDC, dried, water added	cyclohexane	83	94	95	>99
PVPDC, wet, CF_3COOH added[c]	cyclohexane	75	90	96	>99
PVPDC, wet	DMF	38	56	72	86
PVPDC, dry	DMF	5	10	12	-

[a] Reaction of 1.9 g of PVPDC with 8 mmol of benzyl alcohol (molar ratio 1.1:1) in 10 mL of solvent at 70 °C. [b] Determined by GLC. [c] 0.2 mL of trifluoroacetic acid added to 1 g of PVP while preparing the reagent.

Since it became apparent that the commercial resin from Polysciences, Inc., had a very low accessibility we prepared several batches of cross-linked poly(vinylpyridine) by emulsion polymerization in the presence of 1–5% divinylbenzene using various combinations of water-soluble polymers and surfactants to help in the formation of porous beads. The resulting polymer beads were less dense than either the commercial product or our original material. By use of this new poly(vinylpyridine) resin, the accessibility of the reactive sites, and thus the reactivity of the PVPCC reagent, increased noticeably. A study of the reactivity of the reagent led us to two interesting observations. First, the PVPCC could now be used in essentially equimolar amount for the oxidation of primary and secondary alcohols; second, extensive washing of the reagent with water following its preparation by reaction with HCl and CrO_3 resulted in the complete removal of chloride ions from the polymer but did not affect its reactivity.

An alternate nonacidic polymeric reagent, poly(vinylpyridinium dichromate), PVPDC, can be prepared easily by treatment of a poly(vinylpyridine) resin with a slight excess of CrO_3 in water at room temperature. After being washed with water to remove any unbound chromium(VI), the reagent can be used directly, without drying, in oxi-

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Table II. Oxidation of Alcohols with PVPDC[a]

alcohol	% conversion (time) molar ratio[b] 1.1:1	molar ratio[b] 1.7:1
benzyl alcohol	75 (15 min) 96 (2 h) >99 (18 h)	>99 (1 h)
1-phenylethanol	89 (5 h) >99 (24 h)	
cinnamyl alcohol	76 (30 min) 98 (4 h)	
cyclopentanol	69 (24 h)	93 (24 h)
cyclohexanol	47 (24 h) 66 (68 h)	76 (24 h) 93 (68 h)
3-pentanol[c]	76 (68 h)	97 (68 h)
1-butanol[c]	81 (68 h)	>99 (68 h)
1-hexanol[c]		85 (68 h)

[a] Reaction with 1.9 g of PVPDC (wet) in 10 mL of cyclohexane at 70 °C. [b] Molar ratio Cr^{VI}-alcohol. [c] Reaction in sealed tube using hexane as solvent.

dation reactions or be dried in vacuo to a yellow-brown powder which is quite stable to prolonged storage. The infrared spectrum of the polymer confirmed that it was a dichromate[5] and a titration indicated a capacity of 2.3 mmol of $(PVPH)_2{}^+Cr_2O_7{}^{2-}$ per gram (or 4.6 mmol of Cr^{VI}/g), a figure which is in good agreement with the theoretical capacity (2.33 mmol/g) of a fully loaded resin.

It should be noted that the reagent could be prepared and handled safely in molar amounts, a definite advantage over more classical CrO_3-based reagents. In addition, the reagent was obtained in quantitatively yield from poly(vinylpyridine) while yields of 65–70% are routinely obtained in the preparation of the corresponding low-molecular-weight soluble reagent.[5]

Preliminary studies (Table I) on the oxidation of benzyl alcohol showed that best results were obtained by using the wet reagent in a nonpolar solvent such as cyclohexane at 70 °C. As expected, in the absence of water the dry reagent was ineffective, the low conversions reported in Table I for the dry reagent in cyclohexane or DMF being likely due to the presence of some humidity in the reaction medium. The reagent prepared in the presence of trifluoroacetic acid[5] was not more reactive than PVPDC alone and polar solvents such as DMF were less satisfactory than the nonpolar hydrocarbons. Processing of the aldehyde after reaction was greatly facilitated by the fact that no chromium ions were leached from the polymer.[6] The results obtained in the oxidation of a number of different alcohols are reported in Table II. As expected the rate of reaction increased when the molar ratio of Cr^{VI} to alcohol was increased, and very fast reactions could be obtained by using a fourfold excess of the reagent. However, the reagent was still quite effective in almost equimolar amount. As expected, the initial rate of reaction with PVPDC is usually quite high but the reaction slows down as the reactive sites are consumed. It should be noted that, although the reaction times are sometimes quite long, no products of over oxidation were detected with any of the alcohols tested.[7] In cases where quantitative yields were not obtained, the balance of material was unchanged starting alcohol.

Recycling of the reagent can be accomplished by using a simple washing–reactivation procedure in which the spent reagent is washed with acid to remove the spent chromium salts. After regeneration of the poly(vinylpyridine) resin, addition of CrO_3 and H_2O reactivates the PVPDC. A sample of the reagent was carried through five reaction cycles with no loss of oxidizing capacity and only a slight decrease in reaction rate. Loss of polymer during this process was negligible (Table III).

Table III. Recycling of PVPDC[a]

cycle	wt of PVP, g	% conversion at reacn time 30 min	2 h	21 h
1[b]	1.01	84	97	>99
2	1.07	84	94	>99
3	1.05	75	90	>99
4	1.11	75	92	>99
5[c]	0.97	75	85	>99

[a] Reaction with 8 mmol of benzyl alcohol in 10 mL of cyclohexane at 70 °C (molar ratio 1.1:1). [b] A cycle consisted of preparation of PVPDC reagent, reaction with alcohol, washing with 2 N NaOH and 2 N HCl until wash water was clear, drying, and weighing the recovered PVP resin. [c] Weight of recovered PVP after 5th cycle was 1.00 g.

After this project was completed, a new cross-linked poly(4-vinylpyridine) resin became commercially available (Reilly Tar and Chemical Corp.). We have tested this resin, which is prepared by using a procedure similar to ours, in the oxidation of cyclohexanol on a mole scale. The resin performed extremely well (95% conversion) and thus seems to be ideally suited for use in the preparation of poly(vinylpyridinium dichromate).

Experimental Section

4-Vinylpyridine was a gift from Reilly Tar and Chemical Corp.; it was distilled in vacuo immediately before use. Divinylbenzene was from Polysciences, Inc. (technical grade, 55% pure). Poly(ethyleneimine) was obtained from Aldrich Chemical Co., Triton X-200 was a gift from Rohm and Haas Corp., and polypropylene glycol 1025 (average mol wt 1000) was a product of Union Carbide Co. IR spectra were recorded on a Pye Unicam SP 1100 spectrometer. NMR spectra were taken on a Varian T-60, HA-100, or CFT-80 spectrometer. GLC analyses were carried out by using columns of 15% Carbowax 20M on Chromosorb P or 4% SE-30 on Chromosorb G. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

Emulsion Polymerization of 4-Vinylpyridine. The procedure used was a modification of our earlier work.[2] Freshly distilled 4-vinylpyridine (200 mL) in toluene (300 mL) containing 15 mL of divinylbenzene was added to a stirred solution of a 3 g of sodium dodecyl sulfate, 6 mL of Triton X-200, and 1 g of poly(ethyleneimine) in 1.5 L of degassed distilled water. After addition of 8 mL of polypropylene glycol 1025 and 1.5 g of azobis(isobutyronitrile) initiator, the mixture was stirred vigorously while the temperature was raised to 85 °C. Polymer beads started forming rapidly but the mixture was left stirring overnight at 85 °C. After filtration, the polymer beads were washed repeatedly with water, methanol, THF, acetone, dichloromethane, and finally ether. After the residue was dried in vacuo 197 g of off-white PVP beads were obtained.

A suitable cross-linked resin with similar characteristics can be obtained from Reilly Tar and Chemical Corp., cross-linked poly(4-vinylpyridine) (catalogue no. R8050).

Preparation of Poly(vinylpyridinium dichromate). To a suspension of 200 g of cross-linked poly(vinylpyridine) resin in

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[5] Miller, F. A.; Wilkins, C. H. *Anal. Chem.* **1952**, *24*, 1253. Corey, E. J.; Schmidt, G. *Tetrahedron Lett.* **1979**, 399.

[6] A referee has suggested that an alternate procedure would be to use a poly(vinylpyridine) resin to filter the reaction mixture after an oxidation with soluble pyridinium dichromate to remove chromium salts. This procedure was found to be ineffective as ion complexation and ligand exchange do not occur to an appreciable extent in the organic reaction medium.

[7] It has also been suggested that acids, if formed, would be retained by the resin and thus would not be detected. We have tested this hypothesis with both fresh and spent reagent and heptanoic acid. Under the conditions of the reaction, heptanoic acid is not retained by the polymer and can be recovered by filtration of the soluble phase.

2 L of water was added 200 g of chromium trioxide. Formation of the reagent occurred very smoothly and no heat was evolved as the mixture was stirred for several hours. After filtration, the resin was washed repeatedly with water until the filtrate was colorless. In general, the reagent was used without drying. However, the reagent could also be dried in vacuo at 50 °C for storage (typically, 1 g of PVP affords 1.9 g of the dry PVPDC). The dry reagent was found to perform very poorly in oxidation reactions, but its activity could be restored completely by soaking in water prior to use.

Titration[2] of the reagent showed that it contained 14 mequiv of oxidizing agent per gram (or 2.3 mmol of $(PVPH)_2{}^+Cr_2O_7{}^{2-}$ per gram). This indicated that >98% of the pyridine units have been converted into dichromate units. The infrared spectrum of the dry reagent showed bands at 930 and 765 cm^{-1}, characteristic of dichromate ion.[5] Anal. Calcd: Cr, 24.28; N, 6.54. Found: Cr, 23.93; N, 6.67.

Oxidation of Alcohols with PVPDC. The standard procedure involved the reaction of 1.9 g of PVPDC with 5–8 mmol of alcohol in 10 mL of cyclohexane or hexane at 70 °C. The progress of the reaction was monitored by gas chromatography. After completion of the reaction the products could be obtained in the soluble phase by washing of the resin. Scaling up of the reaction to oxidize mole quantities of alcohols could be done easily. Thus, 266 g of PVPDC made from 140 g of poly(vinylpyridine) resin was suspended in 1 L of cyclohexane and 122 g (1 mol) of 1-phenylethanol was added. The reaction mixture was stirred at 65 °C and reaction proceeded rapidly and then slowed down as it neared completion. After 48 h, chromatographic analysis showed no starting material remaining. The reaction mixture was filtered and the spent resin was washed with cyclohexane, ether, and dichloromethane. After distillation of the filtrate, 113 g (94% yield) of pure ketone was obtained.

Although cyclohexane was the solvent of choice, hexane was used in reactions in which low-boiling aldehydes were produced to avoid interference of the solvent peak in the GC analysis. In addition, sealed tubes were used as reaction vessels in these cases to prevent loss of the volatile products.

Titration of spent reagent used to oxidize 8 mmol of benzyl alcohol showed that 18 mequiv of oxidizing agent had been consumed, a value which compares favorably with the theoretical value[8] of 16 mequiv.

Recyling of PVPDC. The dark spent resin could be easily recycled by repeated sequential washings with 2 N HCl and 2 N NaOH until the PVP polymer had returned to its original white color, drying, and reacting with CrO_3 to regenerate the reagent. A 200-g batch of PVP used in a reaction such as the one above was recycled and reused in the oxidation of 1 mol of cyclohexanol to produce a 91% conversion to cyclohexanone. Reactions on a smaller scale were also quite effective with easy recycling of the polymer after each use. For example, a 1-g batch of PVP resin was carried through five successive cycles of formation of reagent, oxidation of 8 mmol of benzyl alcohol, washing, and regeneration with no loss of oxidizing capability and only a small decrease in reaction rate. In addition, the weight of the polymer remained essentially constant throughout, the small variations being due to the varying amounts of chromium salts left in the resin after washing.

Acknowledgment. Financial support of this investigation by the Natural Science and Engineering Research Council of Canada is gratefully acknowledged. In addition thanks are due to Dr. G. Gelbard for a fruitful discussion.

Registry No. Benzyl alcohol, 100-51-6; 1-phenylethanol, 98-85-1; cinnamyl alcohol, 104-54-1; cyclopentanol, 96-41-3; cyclohexanol, 108-93-0; 3-pentanol, 584-02-1; 1-butanol, 71-36-3; 1-hexanol, 111-27-3; benzaldehyde, 100-52-7; 1-phenylethanone, 98-86-2; 3-phenyl-2-propenal, 104-55-2; cyclopentanone, 120-92-3; cyclohexanone, 108-94-1; 3-pentanone, 96-22-0; butanal, 123-72-8; hexanal, 66-25-1; 4-vinylpyridine–divinylbenzene copolymer, 9017-40-7; chromium trioxide, 1333-82-0.

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[8] Gelbard (CNRS, Solaise, France) has informed us that reduction of the polymer-bound chromate or chloroformate may in fact produce Cr^{IV} rather than Cr^{III}. We have made no attempt to characterize fully the reduced species bound to the polymer.

A Novel Rearrangement of Tricyclo[4.2.2.0^{2,5}]deca-3,7-dien-9-ones to Functionalized Bicyclo[3.2.1]octa-2,6-dienes

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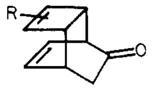
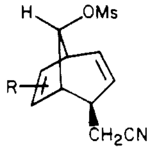
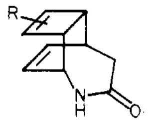
The bicyclo[3.2.1]octa-2,6-diene framework is endowed with many structural features that make it an attractive substrate for synthetic and mechanistic investigations.[1] Conventionally, synthetic entry to this ring system and its derivatives is gained either from bicyclo[2.2.1]hepta-2,5-diene (norbornadiene) via a dihalocarbene addition–ring-expansion sequence[2] or through the thermal $[_\pi2_s + {}_\sigma2_s + {}_\pi2_s]$ (Cope) rearrangement of 6-vinylbicyclo[3.1.0]hex-2-enes.[3] In this communication, we describe a novel entry to the bicyclo[3.2.1]octa-2,6-diene ring system from tricyclo[4.2.2.0^{2,5}]deca-3,7-dien-9-ones (I) and (II) via Schmidt fragmentation and carbonium ion rearrangement. The interesting and useful aspect of this rearrangement is the ready availability[4] of precursors I and II and formation of bicyclo[3.2.1]octanes carrying functionality in all three bridges and in particular at C_8.



I, R = H
II, R = Br



IV, R = H
VIII, R = Br



V, X = H
X, X = Br

Reaction of the tricyclic dienone I, prepared according to the sequence depicted in Scheme I from the COT–acrylonitrile adduct[5] (III), with sodium azide (1 mol equiv) in methanesulfonic acid (MsOH)–methylene chloride and chromatography of the resulting reaction mixture led to the isolation of IV (55%) and V (22%). While the structure of the minor product (V, mp 178 °C), a lactam, could be readily deduced in a straightforward manner, the formulation of IV (mp 65–66 °C) necessitated an incisive analysis of the spectral data. The elemental composition, $C_{11}H_{13}O_3SN$, and IR spectrum of the major product (IV) indicated the presence of a cyano (2250 cm^{-1}) and mesylate ester (1360, 1180 cm^{-1}) moiety. The ^{1}H NMR spectrum indicated the presence of four olefinic protons at δ 6.25 (1 H, dd, J_1 = 6 Hz, J_2 = 3 Hz), 5.75–6.15 (2 H, m), and 5.64 (1 H, $^1/_2$AB, J = 10 Hz) and a proton attached to a carbon bearing the mesylate group at δ 5.05 (1 H, t, J = 5 Hz) besides other expected resonances (see the Experimental

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