References and Notes

(1) This is the fourth communication in this series; studies on transition metal complexes with cyclic carbene ligands. For last paper in series, see ref 5.
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Polymer Supported Reagents. Chromic Acid on Anion Exchange Resins. A Simple and Practical Oxidation of Alcohols to Aldehydes and Ketones

Sir:

Although many useful procedures for oxidation of alcohols to the corresponding carbonyl compounds have been reported,[1] the general problem cannot be considered definitely settled. The chief drawbacks of these procedures are the relative difficulty in the preparation of the reagents and in the working-up of the reaction mixture.

It has been found recently that reagents supported on insoluble polymers are particularly convenient for solving many problems in organic synthesis.[2] The polymeric support provides a particular reaction environment capable of enhancing the reactivity of many reagents, and moreover, turns out to be very profitable in the working-up, which becomes reduced to a mere filtration. Thus, anion exchange resins are, for example, useful in C-alkylation of phenols,[3a] O-alkylation of carboxylate anions,[3b] and alkyl or aralkyl fluorides preparation.[3c] A polymeric thioanisole has been reported[4] to be an effective coreactant for the sulfide-based Corey oxidation of alcohols.[5]

Although this oxidation technique has been demonstrated to be useful in dealing with highly sensitive compounds, specifically for certain prostaglandin intermediates,[4] the whole procedure seems to be somewhat laborious and requires ad hoc prepared polymers.

We have now found that it is possible to obtain in a simple way a polymer supported reagent very useful for the oxidation of alcohols utilizing, without modification, commercial anion exchange resins. To prepare the reagent, 35 g of the chloride form of Amberlyst A-26, a macroreticular anion exchange resin containing quaternary ammonium groups,[6] was added under stirring into a solution of 15 g of chromium trioxide in 100 ml of water.[7] Chloride ions were readily displaced and a CrO_4H^- form of the resin was quantitatively obtained in 30 min. The resin was successively rinsed with water, acetone, and ether and finally dried in vacuo at 50 °C for 5 h.

The capacity of the resin was determined by stirring overnight 0.5 g of the resin with 10 ml of 2 N aqueous potassium hydroxide, filtering off and titrating iodometrically the obtained chromate solution. The determined average capacity of the dried resin was 3.8 mmol CrO_3/g of resin. The resin so obtained did not noticeably lose activity neither on storing in air at room temperature for several weeks nor on refluxing for 5 h in benzene or hexane.

Our polymeric reagent is remarkably effective in oxidizing primary and secondary alcohols to aldehydes and ketones in high yields (Table I). The reaction is simply performed by a

Table I. Oxidation of Alcohols to Aldehydes and Ketones[a]

Alcohol	Ratio mmol substrate/g resin[j]	Reaction time, h	Yield, %
1-Octanol	1/3.5	3	93,[b,d] 94[b,e]
	1/3.5	9	89[e,k]
	1/1.2	9	97[b,e]
1-Dodecanol	1/3.5	3	83,[b,d] 87[b,e]
	1/1.2	9	94[b,e]
1-Tetradecanol	1/3.5	3	93[b,d]
Benzyl alcohol	1/3.5	1	98,[b,g] 96[b,e]
	1/0.75	2	98[b,e]
Cinnamyl alcohol	1/3.5	1	95,[b,g] 96[b,f]
	1/0.75	2	92[b,g]
3-Methyl-2-buten-1-ol	1/3.5	1	91[b,d]
3-Methyl-3-buten-1-ol	1/3.5	3	93[b,d,h]
2-Hendecanol	1/3.5	3	73[b,d]
Cyclohexanol	1/3.5	3	77[b,d]
Geraniol	1/3.5	1	90,[b,d,i] 92[b,e,i]
	1/0.75	2	90[b,e,i]
9-Fluorenol	1/0.75	1	97[c,e]
Menthol	1/3.5	3	86,[b,d] 93[b,e]
	1/1.2	9	91[b,e]
Diphenylcarbinol	1/3.5	1	77[c,e]
2-(Hydroxymethyl)naphthalene	1/3.5	1	90[c,e]
4-Benzensulfonyl-3-methyl-2-buten-1-ol	1/0.75	1	98[c,f]

[a] The reactions were carried out with 2 mmol of alcohol in 15 ml of refluxing solvent. [b] Yield determined by GLC analysis. Column ⅛ in. × 6 ft 20% DEGS. Column temperature, program from 50 to 200 °C at 10 °C/min; injection port, 280 °C; detector, 280 °C; carrier gas, N_2, 1.0 Kg/cm^2. [c] Yield determined on pure isolated products. [d] In hexane. [e] In benzene. [f] In $CHCl_3$. [g] In THF. [h] A mixture of 3-methyl-2-buten-1-al (48%) and 3-methyl-3-buten-1-al (52%) was obtained. [i] *Z–E* isomerization occurs and one obtains a mixture of geranial and neral. [j] The determined average capacity of the dried resin was 3.8 mmol CrO_3/g resin. [k] Yield refering to pure distilled product in a run of 100 mmol of alcohol in 250 ml of refluxing solvent.

batch technique by stirring an excess of the CrO_4H^- resin with the alcohols in a suitable refluxing solvent. The reaction product was then isolated by filtering off the resin and removing the solvent by distillation.

The nature of the solvent does not appear to be particularly critical. Hydrocarbons, chlorinated hydrocarbons, benzene, and ethers are equally effective, the practical choice being oriented by the solubility of the products and the desired reaction temperature. Toluene is less recommendable, owing to small amounts of benzaldehyde formed as by-product. The reaction seems to be quite general, allylic, benzylic, and saturated primary and secondary alcohols being cleanly converted to the corresponding carbonyl compounds in high yields.

No traces of carboxylic acids or other by-products were detected in all the cases studied. The only products isolated were the expected carbonyl compounds and, in the cases where the reaction had not gone to completion, the starting material was recovered.

The products were identified either by comparison with authentic samples or by spectroscopic, mass spectral, and elemental analysis.

The reaction rate depends both on the structure of the alcohol and on the substrate to resin ratio; it is faster for allylic and benzylic alcohols and for higher substrate to resin ratios. Regeneration of the resin in the chloride form is readily accomplished by washing successively with 2 N sodium hydroxide and 1 N hydrochloric acid solution.

The fact that the chromium ions in this reagent remain firmly bound to the resin before and after the reaction may be valuable in preventing environmental pollution.

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(6) Also Amberlyst A-29, Amberlite IRA 400, and Amberlite 904 were successfully employed.
(7) Also column technique has been employed.

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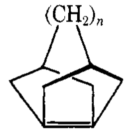
Synthesis of Tricyclo[3.3.3.0^{2,6}]undec-2(6)-ene. A Novel Bridgehead Olefin

Sir:

Several years ago we reported the development of reductive transannular ring closure as an important step in the synthesis of olefins of type **1** from bicyclo[3.3.*n*]alkane-3,7-diones.[1] More recently, we have successfully used this scheme to prepare a derivative of the $n = 2$ member of this series.[2] In this communication we report the synthesis by a similar route of tricyclo[3.3.3.0^{2,6}]undec-2(6)-ene (**2**), a molecule belonging to another class of strained olefins.



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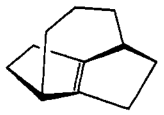
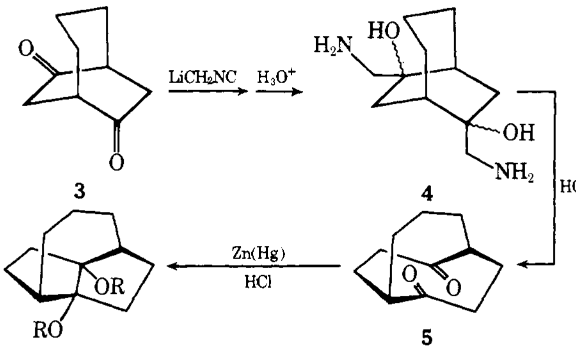


2

The "strain" in the double bond in **2** is quite different from that in the π bonds in molecules of type **1**, where overlap between atomic orbitals is diminished by pyramidalization of the carbons forming the double bonds.[3] Tricyclo[3.3.3.0^{2,6}]undec-2(6)-ene (**2**), in the Wiseman analysis[4] of bridgehead olefins,[5] may be viewed as a bisethano derivative of *trans*-cycloheptene. Although the olefinic carbons in such molecules may be somewhat pyramidalized,[6] overlap between the atomic orbitals forming the π part of the double bond is principally diminished by torsion. The two ethano bridges in **2** serve, of course, to prevent the trans → cis isomerization that occurs in *trans*-cycloheptene.[7] Indeed, Wiseman and Chong have synthesized a mixture of two *trans*-cycloheptene derivatives in which a single ethano bridge prevents isomerization, and they find that these molecules are stable at −70 °C but dimerize on warming to room temperature.[8] The second ethano bridge in **2** might tend to inhibit dimerization, not only by providing additional steric hindrance to cyclobutane ring formation but also by rendering impossible the $_{\pi}2_s + {}_{\pi}2_a$ pathway that has been proposed for the dimerization of some *trans*-cycloalkenes.[9,10]

The required diketone precursor of **2**, bicyclo[3.3.3]undeca-2,6-dione (**5**), was prepared by Tiffeneau-Demjanov ring expansion of bicyclo[3.2.2]nona-6,8-dione (**3**).[11] Of the many reactions investigated for the transformation of **3** to **4**, the most satisfactory proved to be treatment of **3** with excess isocyanomethyllithium (THF, −60 °C, 65% yield), followed by hydrolysis in refluxing methanolic HCl of the diadduct.[12] Although some monoadduct was invariably isolated from the first reaction, it could be separated from the diadduct and recycled. Rearrangement of **4** was effected by addition of sodium nitrite to the crude hydrochloride salt in a two-phase mixture of benzene and buffered acetic acid. This reaction might have led to the diketone precursor of **1**, $n = 3$, by migration of the more substituted carbon atoms. That this was not, in fact, the major reaction path[13] was indicated by the ^1H NMR spectrum ($CDCl_3$) of the crude product, which showed two methine (δ 2.9) and four methylene (δ 2.5) protons on carbons α to the carbonyls. The crude diketone (**5**) was reduced with a zinc amalgam in aqueous HCl[1] to the crystalline diol (**6**),[14] mp 141–144 °C dec, obtained in 58% overall yield from the isocyanomethyllithium diadduct of **3**. The proton decoupled ^{13}C NMR spectrum of the diol showed six singlets (δ 91.11, 44.67, 31.38, 29.29, 27.24, 18.14), corresponding to the six types of



3
4
5
6, R = H
7, R—R = C=S