Oxidation of Alcohols Mediated by a Polymer Supported Potassium Ferrate as an Effective Mild Oxidant

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ABSTRACT: The use of polymeric oxidizing agents simplifies routine oxidation of reactions because it eliminates the traditional purification. In this article, the use of the cross-linked poly (4-vinylpyridine)-supported potassium ferrate as an effective mild polymeric oxidizing agent is described. This reagent is capable of oxidizing organic compounds and can be used as a versatile reagent in organic synthesis. Primary and secondary benzylic and allylic alcohols are converted selectively to their carbonyl compounds, and hydroquinone to the 1, 4-benzoquinone. This polymeric reagent seems to be nontoxic and nonpollutant. Based on our observation during the study, the polymeric reagent is stable and can be stored for months without losing its activity. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 119: 3462–3466, 2011

Key words: oxidation; ferrate; alcohols; polymeric reagents

INTRODUCTION

The selective oxidation of primary and secondary alcohols to their corresponding aldehydes and ketones, respectively, plays a pivotal role in the synthetic organic chemistry,[1] consequently various homogeneous oxidizing reagents have been developed to effect these transformations. However, a major drawback of such oxidants is their lack of selectivity, over-oxidation of aldehydes to carboxylic acids, degradation of unsaturated substrates and their toxicity.[1,2] Due to the poor selectivity and recoverability of these oxidants, attempts were made to anchor the homogeneous oxidant onto a support material, which combine the advantages of both homogeneous and heterogeneous catalysts. The study of polymer-supported reagents and the catalysts is motivated by the major advantage of the physical separation of the supported reagent from the substrates and products, thereby allowing the recycling of expensive catalysts (e.g., noble metals) or of the toxic products and is of prime economic and environment importance,[3,4] supported reagents may also be used more conveniently in excess to drive reactions to completion, without incurring a penalty in the work-up procedures.

The development of the polymer supported oxidants has preceded parallel to the development of the polymeric reagents over the past decades. These reagents can be usually prepared from commercial anion exchange resins or from polymers such as cross-linked poly (vinylpyridine) as support. Among these, the polymer supported chromates,[5,6] chlorochromate,[7] dichromate,[8,9] metal dichromates,[10,11] polymer supported perruthenate,[12] poly (4-vinylpyridine)-supported sodium ruthenate,[13] and poly (4-vinylpyridine) supported potassium bromate,[14] have special places, and have been used for oxidation of a variety of organic compounds.

Manganate, chromate, and ferrate anions are structurally similar species and can be used as an oxidizing agent. Ferrate ion has been identified as an effective mild oxidant and this unusual species shows great promise as a potential alternative to more toxic, less selective oxidizing agents. Although there are some inorganic and organic reactions which used metal ferrate as an oxidizing reagent,[15–22] but to the best of our knowledge, there is no report on the polymer-supported potassium ferrate for the oxidation of organic compounds. Kim et al.[23] reported the selective oxidation of activated alcohols using a solid mixture of potassium ferrate, alumina, and copper sulfate pentahydrate.

Recently, Laszlo and Delaude[24] have reported the ferrate-mediated oxidation of alcohols using a nonaqueous solvent with a montmorilonite clay catalyst.

In continuing of our studies on the development of application of cross-linked poly (4-vinylpyridine) in organic synthesis,[14,25–33] herein we report synthesis and application of cross-linked poly (4-vinylpyridine) supported potassium ferrate, [P$_4$-VP] FeO$_4$, as a green, clean, and stable polymer supported

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TABLE I
Oxidation of Alcohols Using [P_4-VP] FeO_4 in n-Hexane Under Reflux Conditions

Entry	Substrate	Product[a]	Time (h)	Yield[b] (%)
1	C₆H₅—CH₂OH	C₆H₅—CHO	6	90 (±1)
2	C₆H₅—CH₂OH	C₆H₅—CHO	6	89 (±2)[c]
3	O₂N—C₆H₄—CH₂OH	O₂N—C₆H₄—CHO	3	95 (±1)
4	Cl—C₆H₄—CH₂OH	Cl—C₆H₄—CHO	6	92 (±1)
5	2-Cl-C₆H₄—CH₂OH	2-Cl-C₆H₄—CHO	12	85 (±0.0)
6	2,4-Cl₂-C₆H₃—CH₂OH	2,4-Cl₂-C₆H₃—CHO	14	80 (±1)
7	MeO—C₆H₄—CH₂OH	MeO—C₆H₄—CHO	12	85 (±1)
8	HO—C₆H₄—CH₂OH	HO—C₆H₄—CHO	10	90 (±1)
9	(CH₃)₂N—C₆H₄—CH₂OH	(CH₃)₂N—C₆H₄—CHO	12	88 (±2)
10	t-Bu—C₆H₄—CH₂OH	t-Bu—C₆H₄—CHO	6	87 (±1)
11	Ph-CH(OH)-CH₃	Ph-C(O)-CH₃	7	82 (±1)
12	Ph-CH(OH)-Ph	Ph-C(O)-Ph	5	95 (±1)
13	furyl—CH₂OH	furyl—CHO	8	87 (±1)
14	cinnamyl CH₂OH	cinnamyl CHO	16	82 (±2)
15	HO—C₆H₄—OH	O=C₆H₄=O	2[d]	90 (±0.0)
16	C₆H₅—CH₂CH₂OH	No reaction	48	0.0
17	C₆H₅—CH₂CH₂CH₂OH	No reaction	48	0.0
18	cyclohexyl—OH	No reaction	48	0.0

[a] The structure of all products was confirmed by comparison of their melting point, boiling point, and FT-IR, ^{1}H-NMR and ^{13}C-NMR spectra with those of pure compounds.

[b] Average isolated yields of three times.

[c] In this case, we used polymeric reagent that was stored in our laboratory for three months.

[d] In this case, the reaction was performed at room temperature.

potassium ferrate for conversion of primary and secondary benzylic or allylic alcohols to their aldehydes and ketones under aprotic, and heterogeneous conditions. By using this polymeric oxidizing reagent, many problems associated with metal ferrate oxidizing agent, such as the necessity of having a strong basic solution, and instability of metal ferrate[34] has been overcome.

EXPERIMENTAL

Chemical

All chemical substrates were either prepared in our laboratory or were purchased from Fluka, chemical Co. (Buchs, Switzerland), Aldrich chemical Co. (Milwaukee, Wl) and Merck chemical Co. (Germany). Poly (4-vinylpyridine) cross-linked with 2% DVB was commercially product (Fluka). Potassium ferrate

was prepared with high purity (99%) by the oxidation of ferric nitrate with hypochlorite according to the procedure described by Thompson and Schereyer.[35] Poly (N-methyl-4-vinylpyridinium) iodide was prepared according to our procedure.[26,27] Progress of the reaction was followed by TLC using silica gel Poly Gram SIL G/UV 254 plates. All products were characterized by comparison of their FT-IR, ^{1}H-NMR and ^{13}C-NMR spectra, TLC, and physical data with pure compounds. All yields refer to the isolated products. FT-IR, ^{1}H-NMR and ^{13}C-NMR spectra were run on a Bruker, Equinox (model 55) and Bruker AC 500, Aveance DPX spectrophotometer, respectively (using tetramethylsilane as internal reference).

Preparation of [P_4-VP] FeO_4

To an alkali solution (PH: 9–10) of potassium ferrate (0.8 g in 10 mL of distilled water), 1 g of poly (N-methyl-4-vinylpyridinium) iodide was added and slowly stirred for 24 h. Poly (4-vinylpyridine) supported potassium ferrate, [P_4-Met] FeO_4, was filtered off and washed rapidly with distilled water until the filtrate gave a negative test for ferrate ion then it was dried under vacuum in the presence of P_2O_5 at 40°C. The capacity of the polymer was determined by potentiometric titration of filtrates with a 0.1N solution of silver nitrate. The activity of polymer was found to be 2.5 mmol per g of the polymer.

General procedure for oxidation of primary or secondary alcohols using [P_4-VP] FeO_4

To a mixture of primary or secondary alcohol (1 mmol) and n-hexane (10 mL) in a round-bottomed flask (50 mL), 1 g of poly (4-vinylpyridine) supported potassium ferrate was added, and the mixture was stirred under reflux conditions for the time specified in Table I. The progress of the reaction was monitored by TLC (n-hexane : ethyl acetate) (20 : 1). On completion of reaction, the mixture was filtered, and the solvent was evaporated to obtain pure aldehydes or ketones in high yields (80–95%) (Table I). The spend polymer was regenerated by treatment with a potassium ferrate solution.

Preparation of 4-nitrobenzaldehyde from 4-nitrobenzylalcohol: A typical procedure

To a mixture of 4-nitrobenzylalcohol (153 mg, 1 mmol) and n-hexane (10 mL) in a round-bottomed flask (50 mL), 1 g of poly (4-vinylpyridine) supported potassium ferrate was added, and the mixture was stirred under reflux conditions for 3 h. The progress of the reaction was monitored by TLC (n-
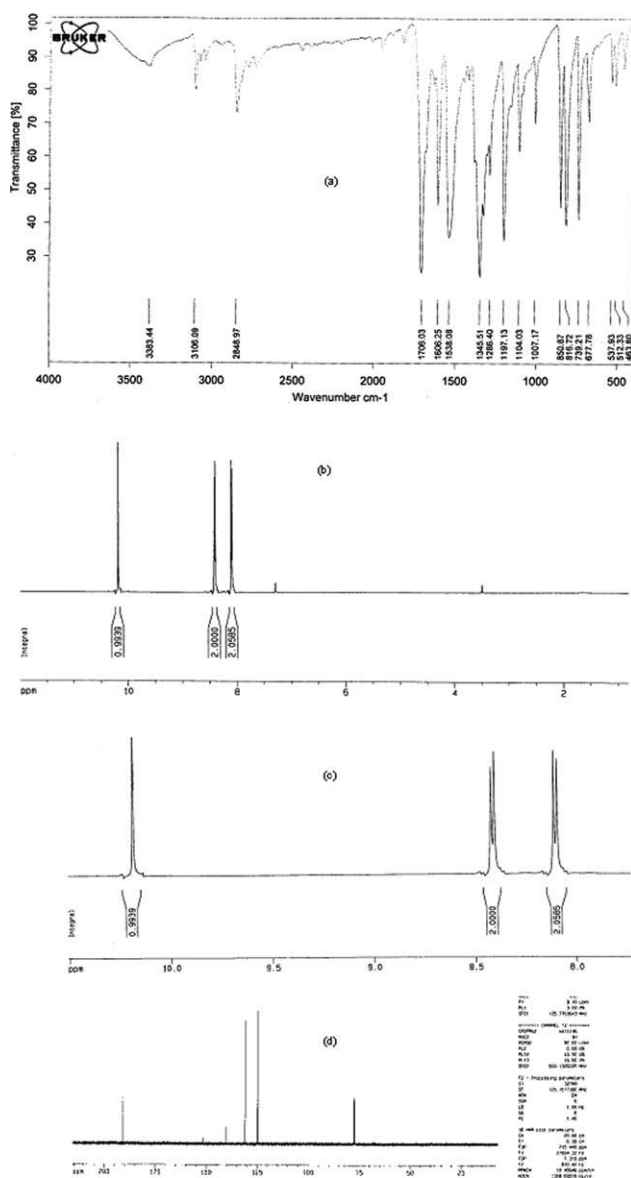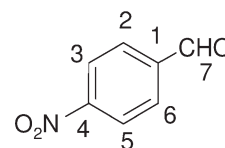
Figure 1 FT-IR (a), ^{1}H-NMR (b), expanded ^{1}H-NMR (c), and ^{13}C-NMR (d) spectra of p-nitrobenzaldehyde.

Mp = 102–104°C (lit,[36] mp: 106°C); FT-IR (KBr) ν (cm^{-1}): 1706 (C=O), 1345 and 1538 cm^{-1} (NO$_2$). ^{1}H-NMR (500 MHz, CDCl$_3$) δ (ppm): 8.105 (d, 2H, H2, and H6, J = 8.5 Hz), 8.414 (d, 2H, H3, and H5, J = 8.5 Hz), 10.186 (S, 1H, H7). ^{13}C-NMR (125 MHz, CDCl$_3$) δ (ppm): 124 (C3 and C5), 130 (C2 and C6), 140 (C1), 151(C4), 190 (C6). The FT-IR, ^{1}H-NMR and ^{13}C-NMR spectra of product (p-nitrobenzaldehyde) are given in Figure 1.

RESULTS AND DISCUSSION

In this study, the solution of potassium ferrate as the precursor for the preparation of the polymer supported potassium ferrate is directly used. In general, there are three methods for the synthesis of potassium ferrate: (1) the electrochemical method, by which anodic oxidation uses iron or alloy as the anode and NaOH/KOH as the electrolyte; (2) the dry method, by which various of iron oxide-containing minerals are heated or melted under strong alkaline conditions and with oxygen flow; (3) the wet method, by which a Fe(III) salt is oxidized under strong alkaline conditions and either hypochlorite or chlorine is used as an oxidant. The third approach is widely considered to be the most practical. In this study, potassium ferrate was prepared according to Thompson and Schereyer method,[35] (a wet method). In this case, potassium ferrate is prepared according to Scheme 1.

Poly(4-vinylpyridine) supported potassium ferrate, [P$_4$-VP] FeO$_4$, is easily prepared by treatment of cross-linked poly(N-methyl-4-vinylpyridinium) iodide, (II), with an alkali solution of potassium ferrate in water, at room temperature [eq. (2) in Scheme 2]. [P$_4$-VP] FeO$_4$ is used as a clean, simple, and selective oxidizing reagent for primary or secondary benzylic alcohols in n-hexane at reflux conditions. In these reactions, primary benzylic alcohols are converted to aldehydes, and secondary benzylic alcohols are converted to their ketones in good to high yields and benzoic acid byproduct was not observed

hexane : ethyl acetate) (20 : 1). On completion of reaction, the mixture was filtered, and the solvent was evaporated to obtain pure 4-nitro-benzaldehyde (143 mg, 95% yield). The melting point, FT-IR, ^{1}H-NMR and ^{13}C-NMR spectra data of product are given below and for specification of the peaks at corresponding atoms and numbered.
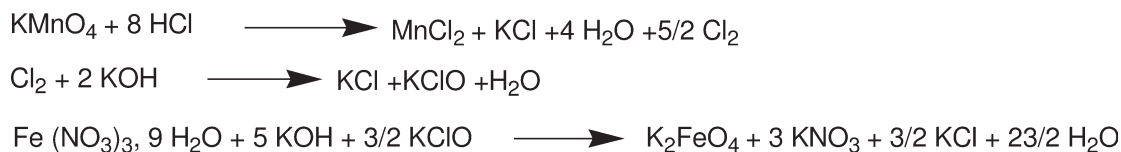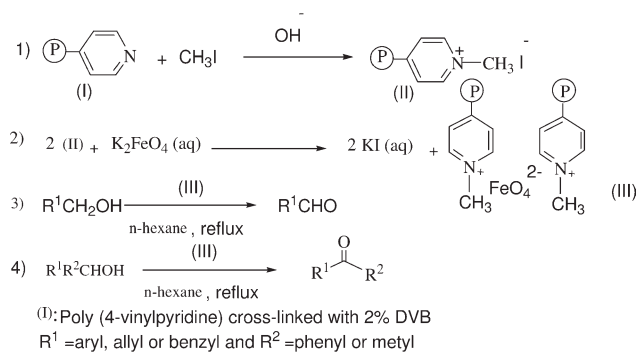
KMnO$_4$ + 8 HCl $\longrightarrow$ MnCl$_2$ + KCl +4 H$_2$O +5/2 Cl$_2$

Cl$_2$ + 2 KOH $\longrightarrow$ KCl +KClO +H$_2$O

Fe (NO$_3$)$_3$, 9 H$_2$O + 5 KOH + 3/2 KClO $\longrightarrow$ K$_2$FeO$_4$ + 3 KNO$_3$ + 3/2 KCl + 23/2 H$_2$O

Scheme 1 Preparation of potassium ferrate.

Scheme 2 Preparation of polymer-supported potassium ferrate and oxidation of alcohols.

[eqs. (3) and (4) in Scheme 2]. $[P_4\text{-VP}]FeO_4$ does not irritate mucous membrane and skin. Also $[P_4\text{-VP}]FeO_4$ is a cross-linked polymer therefore, it is nonvolatile and seems to be a nontoxic and nonpollutant polymeric reagent.

The structure of all of the products was confirmed by comparing their boiling point, melting point, FT-IR, ^{1}H-NMR and ^{13}C-NMR spectra with pure compounds. The advantages of the method are: (1) the reaction can be performed in nonaqueous medium; (2) an excess of the reagent can be used; (3) separation of the product is very easy, and can be obtained by simple filtration and evaporation of the solvent; (4) no waste or by-products are formed; and (5) The method can be used for selective oxidation of benzylic alcohols. Also, based on our observation during the study, the polymeric reagent is stable and can be stored for months without losing its activity (entry 2 in Table I).

Optimization of the reaction conditions showed that for most of the reactions, n-hexane at reflux conditions give the best results and the best molar ratio of the oxidant to substrate is 2.5. All the reactions were performed under reflux conditions except, hydroquinone that oxidized at room temperature (entry 15 in Table I). The scope and generality of

this process is illustrated with several example of primary and secondary saturated, benzylic alcohols, and the representative results are summarized in Table I. This polymeric reagent is effective mild and selective oxidizing reagent and can only oxidize the primary and secondary benzylic alcohols, to corresponding carbonyl compounds and, primary or secondary saturated alcohols remained intact in the reaction mixture after 48 h, as an example, the results of oxidation of 2-phenyl ethanol, 3-phenyl propanol, and cyclohexanol that were not oxidized are shown in Table I (entries 16–18). The oxidizing reagent is able to oxidize primary benzylic alcohols to corresponding aldehydes and secondary benzylic alcohols to corresponding ketones. As seen in Table I, the presence of an electron acceptor group on the ring of benzyl alcohols decreases the reaction time, and the presence of electron realizing group or substituted group on orto position of the ring increases the reaction time (Table I). From these results it can be concluded that, in the following proposed mechanism, the formation of carbon radical intermediate is slow, but the further oxidation that gives a carbocation intermediate is fast (Scheme 3).

The most comprehensive study on the mechanism of potassium ferrate mediated oxidation of alcohols was carried out by Lee and Gai,[34] consistent with this work is the mechanism presented below which involve C—H insertion of a Fe=O bond to generate a Fe—C bond. Homolysis of this bond leads to a carbon radical which, on further oxidation gives the resulting carbonyl containing product via a cationic species (Scheme 3).

To demonstrate the selectivity of this method, a competitive reaction was performed between benzyl alcohol and 2-phenyl ethanol. It was observed that benzaldehyde is only product in 90% yield, and 2-phenyl ethanol remained intact in the reaction mixture after 6 h (Scheme 4).

Based on the above mechanism, when the carbon radical formation step is the rate determining step, it
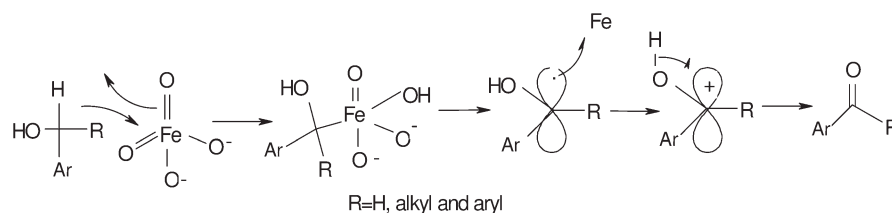
Scheme 3 Mechanism of ferrate ion mediated oxidation of alcohols.
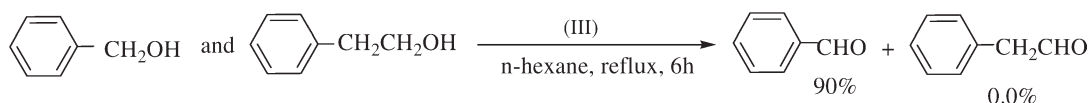
Scheme 4 Competitive reaction of benzyl alcohol and 2-phenyl ethanol.

can be oncluded that the formation of the stable benzyl radical is faster than primary radical. Thus, benzaldehyde is the only product and 2-phenyl ethanol remains intact.

To demonstrate the stability of polymeric reagent we used the [P$_4$-VP] FeO$_4$ that stored in our laboratory for 3 months, for oxidation of benzyl alcohol, and the results are given in Table I (entry 2). As it can be seen, the results are the same as freshly prepared [P$_4$-VP] FeO$_4$.

References

1. Friedrich, H. B. Platinum Metals Rev 1999, 43, 94.
2. Heravi, M. H.; Ajami, D.; Aghapoor, K.; Chassemzadeh, M. Chem Commun 1999, 833.
3. Tsonis, C. P. J Chem Ed 1984, 61, 479.
4. Guyot, A. Pure Appl Chem 1988, 60, 365.
5. Cainelli, G.; Cardillo, G.; Osena, G.; Andri, S. J Am Chem Soc 1976, 98, 6737.
6. Cardillo, G.; Orena, M.; Sandri, S. Tetrahedron Lett 1976, 17, 3985.
7. Frechet, J. M. J.; Warnock, J. Farrall, M. J. J Org Chem 1978, 43, 2618.
8. Frechet, J. M. J.; Darling, P.; Farrall, M. J. J Org Chem 1981, 46, 1728.
9. Tamami, B.; Goudarzian, N. Eur Polym J 1992, 28, 1035.
10. Firouzabadi, H.; Tamami, B.; Goudarzian, N.; Hatam, M.; Mansour Lakouraj, M. Synth Commun 1991, 21, 2077.
11. Tamami, B.; Hatam, M.; Mohadjer, D. Polym Bull 1989, 21, 531.
12. Hinzen, B.; Ley, S. V. J Chem Soc Perkin Trans 1, 1997, 1907.
13. Holger, B. F.; Nirad, S. Tetrahedron Lett 2000, 41, 3971.
14. Tamami, B.; Karimi Zarchi, M. A. Eur Polym J 1995, 31, 715.
15. Tsuda, Y.; Nakazima, S. Chem Lett 1978, 1397.
16. Kim, K. S.; Chang, Y. K.; Bae, S. K.; Halai, C. S. Synthesis 1984, 866.
17. Caddick, S.; Murtagh, L.; Weaving, R. Tetrahedron 2000, 56, 9373.
18. Audette, R. J.; Quail, J. W.; Smith, P. J. Tetrahedron Lett 1971, 11, 279.
19. Sharma, V. K.; Mishra, S. K.; Nesnas, N. Environ Sci Technol 2006, 40, 7222.
20. Sharma, V. K.; Rendon, R. A.; Millero, F. J.; Vazquez, F. G. Mar Chem 2000, 70, 235.
21. Ohta, T.; Kamachi, T.; Shiota, Y.; Yoshizawa, K. J Org Chem 2001, 66, 4122.
22. Huang, H.; Sommerfeld, D.; Dunn, B. C.; Eyring, E. M.; Lloyd, C. R. J Phys Chem A 2001, 105, 3536.
23. Kim, K. S.; Song, Y. H.; Hahn, C. S. Tetrahedron Lett 1986, 25, 2875.
24. Laszlo, P.; Delaude, L. J Org Chem 1996, 61, 6360.
25. Tamami, B.; Iranpoor, N.; Karimi Zarchi, M. A. Polymer 1993, 34, 2011.
26. Karimi Zarchi, M. A.; Zarei, A. J Chin Chem Soc 2005, 52, 309.
27. Karimi Zarchi, M. A.; Noei, J. J Appl Polym Sci 2007, 104, 1064.
28. Karimi Zarchi, M. A. J Chin Chem Soc 2007, 54, 1299.
29. Karimi Zarchi, M. A.; Mirjalili, B. F.; Ebrahimi, N. Bull Korean Chem Soc 2008, 29, 1079.
30. Karimi Zarchi, M. A.; Noei, J. J Appl Polym Sci 2009, 114, 2134.
31. Karimi Zarchi, M. A.; Bahadoran, A. J Appl Polym Sci, 2010, in press.
32. Karimi Zarchi, M. A.; Mirjalili, B. F.; Shamsi Kahrizsangi, Z.; Taefi, M. J Iran Chem Soc, 2010, 7, 455.
33. Karimi Zarchi, M. A.; Mirjalili, B. F.; Kheradmand Aval, A. J Appl Polym Sci 2010, 115, 237.
34. Lee, D. G.; Gai, H. Can J Chem 1993, 71, 1394.
35. Thompson, L. T. O.; Schereyer, J. M. J Am Chem Soc 1950, 73, 1379.
36. Shriner, R. L.; Fuson, I. R. C.; Curtin, D. Y.; Morrill, T. C. The Systematic Identification of Organic Compounds, 6th ed.; Wiley: New York, 1980.