Ultrasound-Mediated Preparation and Applications of Chromyl Chloride[1]

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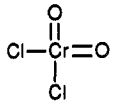
The use of chromyl chloride (1) as a reagent may be traced to the original studies of Étard in which the C–H bonds of hydrocarbons were observed to be oxidized to carbonyl groups.[2] Since that time the scope of chromyl chloride as an oxidant has expanded considerably and includes the conversion of olefins to epoxides,[3] carbonyl compounds,[4] chlorocarbonyl compounds,[5] and keto alcohols[6] as well as the preparation of chromate esters[7] for use in the oxidation of secondary alcohols to the corresponding carbonyl compounds. As part of a program directed toward



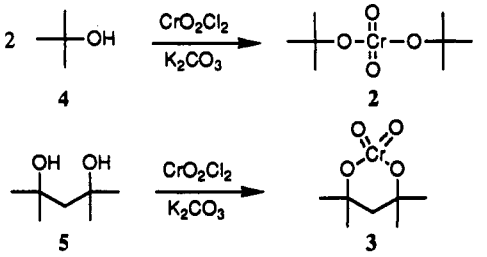
1

the preparation of a series of novel chromate esters as oxidation reagents, we required a facile inexpensive route to large amounts of chromyl chloride. Inspection of the literature revealed several laboratory-scale preparations of 1, including the treatment of chromium trioxide with acetyl chloride, phosphorus pentachloride, or hydrogen chloride.[8] Although many of the previously described preparations are inexpensive, these procedures are often undesirable since difficult purifications involving complex mixtures and acidic byproducts are often encountered.[9] A particularly attractive disclosure described the treatment of chromium trioxide with titanium(IV) chloride (1:1, neat; 100–150 °C; 1–8 h) followed by distillation (eq 1).[10] We

$$2CrO_3 + TiCl_4 \rightarrow 2CrO_2Cl_2 + TiO_2 \qquad \text{eq. 1}$$

found this reaction suitable for our purposes since inert titanium dioxide is formed as a byproduct and 1 may be easily separated by atmospheric or vacuum distillation if so desired. In adapting and improving the protocol for our use we required abbreviated reaction times in addition to a reaction solvent which would also be suitable for subsequent reactions. Given that chromium trioxide is insoluble in both carbon tetrachloride and dichloromethane, the irradiation of a chromium trioxide and titanium(IV) chloride (2:1) mixture with ultrasound in either solvent for 2–3 h at room temperature results in the complete consumption of reactants and formation of the red-brown solution of 1 and precipitated titanium dioxide. While the original protocol required a neat mixture of chromium trioxide and titanium(IV) chloride,[11] we find that using a reaction solvent such as dichloromethane or carbon tetrachloride is the best expedient since solutions of the freshly-prepared reagent may be manipulated immediately or substrates and coreactants may be added directly to solutions of 1.

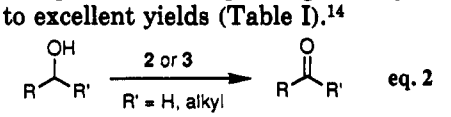
Scheme I



4 2

5 3

The convenience and versatility of the ultrasonically-prepared chromyl chloride was first demonstrated by facile conversion to the corresponding chromate ester oxidants 2 and 3 by addition of 1 directly to a solution of *tert*-butyl alcohol (4) or 2,4-dimethylpentane-2,4-diol (5) in dichloromethane or carbon tetrachloride in the presence of anhydrous potassium carbonate (Scheme I). While the efficacy of 2 and 3 as both stoichiometric and catalytic reagents in the oxidation of organic substrates has been established,[12,13] we elected to confirm the reactivity of 2 and 3 without the removal of the potassium carbonate buffer system (Scheme I) or the precipitated titanium dioxide (eq 1). In this connection, the reactivity of 2 or 3 as a system was demonstrated by its facile use in the oxidation of various primary and secondary alcohol substrates (eq 2) to the corresponding carbonyl compounds in good to excellent yields (Table I).[14]



eq. 2

(1) Ultrasound in Oxochromium(VI)-Mediated Transformations. 2. For Part 1, see: Adams, L. L., Luzzio, F. A. *J. Org. Chem.* **1989**, *54*, 5387.

(2) (a) Étard, A. *Compt. Rend.* **1877**, *84*, 127. (b) Étard, A. *Ann. Chim. Phys.* **1881**, *22*, 218. (c) Cainelli, G.; Cardillo, G. *Chromium Oxidations in Organic Chemistry*; Springer-Verlag: Berlin, 1984; p 33. (d) Wheeler, O. H. *Can. J. Chem.* **1958**, *36*, 667. (e) Wiberg, K. B.; Marshall, B.; Foster, G. *Tetrahedron Lett.* **1962**, *8*, 345. (f) Necsoiu, I.; Balaban, A. T.; Pascaru, I.; Sliam, E.; Elian, M.; Nenitzescu, C. D. *Tetrahedron* **1963**, *19*, 1133. (g) Rentea, C. N.; Rentea, M.; Necsoiu, I.; *Tetrahedron* **1968**, *24*, 4667. (h) Hartford, W. H.; Darrin, M. *Chem. Rev.* **1958**, *58*, 1.

(3) Miyaura, N.; Kochi, J. K. *J. Am. Chem. Soc.* **1983**, *105*, 2368. Rappe, A. K.; Goddard, W. A. *J. Am. Chem. Soc.* **1980**, *102*, 5115. Sharpless, K. B.; Flood, T. C. *J. Am. Chem. Soc.* **1971**, *93*, 2316. Bachelor, F. W.; Cheriyan, U. O. *Can. J. Chem.* **1976**, *54*, 3383. Bachelor, F. W.; Cheriyan, U. O. *J. Chem. Soc., Chem. Commun.* **1973**, 195.

(4) Freeman, F.; Cameron, P. J. *J. Org. Chem.* **1968**, *33*, 3970. Freeman, F.; DuBois, R. H.; Yamachika, N. J. *Tetrahedron* **1969**, *25*, 3441. Freeman, F.; Yamachika, N. J. *J. Am. Chem. Soc.* **1972**, *94*, 1214.

(5) Sharpless, K. B.; Teranishi, A. Y. *J. Org. Chem.* **1973**, *38*, 185.

(6) Lee, T. V.; Toczec, J. *Tetrahedron Lett.* **1982**, *23*, 2917.

(7) Oppenhauer, R. V.; Oberrauch, H. *An. Asoc. Quim. Argent.* **1949**, *37*, 246. Sharpless, K. B.; Akashi, K. *J. Am. Chem. Soc.* **1975**, *97*, 5927. Suggs, J. W. Ph.D. dissertation, Harvard University, 1976, p 117. Corey, E. J.; Barrette, E. P.; Magriotis, P. *Tetrahedron Lett.* **1985**, *26*, 5855.

(8) Udy, M. J. *Chromium, Chemistry of Chromium and Its Compounds*; Reinhold: New York, 1956; Vol I, pp 191–192.

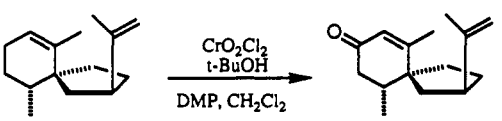
(9) (a) Flesch, G. D.; Svec, H. J. *J. Am. Chem. Soc.* **1958**, *80*, 3189. (b) Sisler, H. H. In *Inorganic Syntheses*; Fernelius, W. C., Ed.; McGraw-Hill: New York, 1946; Vol. II, pp 205–207.

(10) Braos, H.; Cohen, H. J. National Distillers and Chemical Corp. US Patent US 3,111,380, Nov 19, 1963.

(11) The original disclosure (ref 10) described a *1:1* mixture of titanium(IV) chloride and chromium trioxide at 130 °C (6 h).

(12) (a) Catalytic: Muzart, J. *J. Chem. Rev.* **1992**, *92*, 113. (b) Stoichiometric: Luzzio, F. A. Unpublished results.

(13) Recently an example of selective allylic oxidation using *tert*-butyl chromate was reported in the final step of the total synthesis of (−)-solavetivone (Hwu, J. R.; Wetzel, J. M. *J. Org. Chem.* **1992**, *57*, 922) as shown:

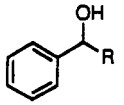
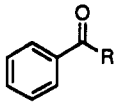
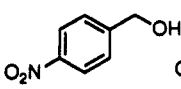
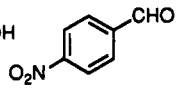
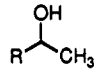
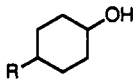
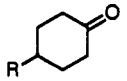


71%

(14) In preparing the ditertiary chromate esters, potassium carbonate appeared to be superior to pyridine, the presence of which slowed the subsequent oxidation considerably.

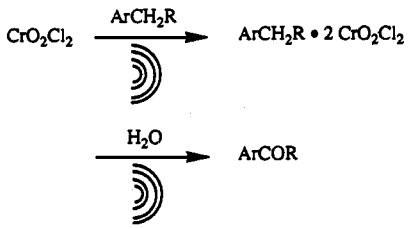
0022-3263/93/1958-0512$04.00/0

Table I. Chromate Ester–Mediated Oxidations of Alcohols

entry	alcohol	product	R	% yield[a,b]
1			CH_3	88 (71)[c]
2			Ph	99[d]
3				96 (84)[c]
4			$n\text{-}C_6H_{13}$	77[c]
5			t-Bu	90[d]
6			Ph	96 (10)[d]

[a] Yields are of isolated products. [b] Yields in parentheses utilized pyridine in chromate ester formation. [c] Oxidations were performed with the *tert*-butyl chromate ester. [d] Oxidations were performed with the cyclic chromate ester.

Scheme II



Attention was then turned to the adaptation of the ultrasound protocol to the Étard oxidation of arylalkanes (Scheme II).[15a] The classical Étard oxidation of benzylic C–H bonds first entails the exothermic addition of the substrate to solutions of chromyl chloride and results in the formation of the putative Étard addition complex.[15b] The adduct, which appears as an amorphous precipitate, is not isolated but is hydrolyzed under aqueous reducing conditions to provide the desired product. Typically the entire operation is conducted in one flask with the adduct formation step utilizing inert solvents such as carbon disulfide, carbon tetrachloride, or chloroform followed by the hydrolysis step which employs an aqueous solution of sodium bisulfite or an aqueous suspension of zinc dust. The hydrolysis converts the adduct to the desired oxygenated compound while the reducing agent reacts with excess chromium(VI) to prevent overoxidation of the desired product. Previous workers have observed inconveniently lengthy reaction times associated with the initial adduct formation step and have recommended long periods of refluxing in order to complete the formation of this species.[16] We find that ultrasound accelerated the formation of the Étard adduct 2-fold after addition of representative arylalkane substrates directly to a solution of freshly-prepared chromyl chloride. In this series of experiments ultrasonically-prepared 1 was used directly and without removal of the precipitous titanium dioxide. Following the formation of the Étard adduct, which

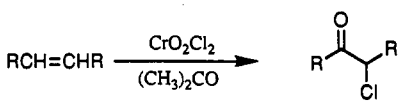
Table II. CrO_2Cl_2-Mediated Oxidations

entry	substrate	product	% yield[a,b]
1	diphenylmethane	benzophenone	99 (80)
2	triphenylmethane	triphenylcarbinol	99 (75)
3	indan	1-Indanone	80 (45)
4	(*E*)-2-octene	3-chloro-2-octanone 2-chloro-3-octanone	65 (77)[c]

[a] Yields for nonsonicated experiments are in parentheses. [b] Yields are of isolated products in both sonicated and nonsonicated experiments. [c] Yields are of a 1:1 mixture of isomers.

appeared as a precipitate, ultrasound was employed in the sodium bisulfite- or zinc-promoted reduction/hydrolysis step which was a two-phase system and particularly amenable to sonication due to efficient mixing and rapid breaking of emulsions.[17]

Freeman and Sharpless have investigated the synthetic and mechanistic aspects of the Étard-type sequence as applied to *olefins*.[18] Depending on solvent and temperature the typical products of the reaction of 1 with cyclic and acyclic olefins are epoxides, chlorohydrins, and vicinal dichlorides.[19] Sharpless and Teranishi have described a preparation of α-chloro ketones from the treatment of olefins with chromyl chloride in acetone followed by zinc dust reduction or sodium bisulfite treatment prior to workup (eq 3).[5] We included ultrasound in the Sharpless–



eq. 3

Teranishi protocol when oxidizing *trans*-2-octene to a mixture of 3-chloro-2-octanone and 2-chloro-3-octanone directly with ultrasound-produced chromyl chloride and without removal of the byproduct titanium dioxide. The substrates, products, and yields of the Étard-type oxidations are presented in Table II.

The reaction-rate enhancement of the ultrasound-promoted chromyl chloride preparation is attributed to phenomena which involve activation of the chromium trioxide particles by localized erosion and microfragmentation.[20] Both processes, which result in surface area alteration, are a consequence of cavitation and shock wave-induced interparticle collisions and thus change the size, surface area, and morphology of the chromium trioxide particles. In turn, the solubility rate of chromium trioxide in the solution of the titanium(IV) coreactant and the chlorinated reaction solvent is increased which results in accelerated formation of 1. Ultrasound accelerated the formation of the Étard adduct by factors which are general to homogeneous sonochemical processes.[21] Efficient mixing and localized heating caused by rapid cavitation-induced implosion have combined to achieve a higher reaction rate in adduct formation. The subsequent two-

(15) (a) Wiberg, K. B. *Oxidation in Organic Chemistry*; Academic Press: New York, 1965; Part A, p 95. See ref 2h and references cited therein. Freeman, F. In *Organic Syntheses by Oxidation with Metal Compounds*; Miss, W. J., De Jonge, C. R. H. I., Eds.; Plenum Press: New York, 1986; p 41. (b) The structure of the Étard complex or Étard adduct is the subject of much speculation; cf. Nenitzescu, C. D. *Bull. Soc. Chim. Fr.* **1968**, 1349. See also ref 2d,e,h.

(16) See ref 2d.

(17) Suslick, K. S. *Sci. Am.* **1989**, *260*, 80. Suslick, K. S. *Science (Washington, D.C.)* **1990**, *247*, 1373.

(18) (a) Freeman, F.; Cameron, P. J.; DuBois, R. H. *J. Org. Chem.* **1968**, *33*, 3970. (b) Freeman, F.; Yamachika, N. J. *Tetrahedron Lett.* **1969**, 3615. (c) Freeman, F.; McCart, P. D.; Yamachika, N. J. *J. Am. Chem. Soc.* **1970**, *92*, 3730. (d) Freeman, F.; Arledge, K. W. *J. Org. Chem.* **1972**, *37*, 2656. (e) Freeman, F.; Yamachika, N. J. *J. Am. Chem. Soc.* **1970**, *92*, 4621. (f) Sharpless, K. B.; Teranishi, A. Y.; Backvall, J. E. *J. Am. Chem. Soc.* **1977**, *99*, 3120.

(19) Gatzke, A. L.; Stairs, R. A.; Diaper, D. G. M. *Can. J. Chem.* **1968**, *46*, 3695. See also ref 18f.

(20) Suslick, K. S.; Johnson, R. E. *J. Am. Chem. Soc.* **1984**, *106*, 6856. Suslick, K. S.; Casadonte, D. J.; Green, M. L. H.; Thompson, M. E. *Ultrasonics* **1987**, *25*, 56. Suslick, K. S.; Casadonte, D. J. *J. Am. Chem. Soc.* **1987**, *109*, 3459. Suslick, K. S.; Doktycz, S. J. *Chem. Mater.* **1989**, *1*, 6. Suslick, K. S.; Doktycz, S. J. *J. Am. Chem. Soc.* **1989**, *111*, 2342.

phase hydrolysis step is greatly facilitated in that the rate depends on the sonochemical development of a rapid biphasic microdispersion. Continuation of ultrasound studies in connection with other types of oxochromium(VI)-mediated transformations is currently in progress and will be reported in due course.

Experimental Section

General Procedures. Products were characterized by comparison of boiling points, melting points, and NMR spectra with those found in literature. Melting points are uncorrected. CH_2Cl_2 was distilled from CaH_2 and stored over 4A molecular sieves prior to use as a reaction solvent. All other reaction solvents were used as commercially supplied. Chromatography solvents were ACS reagent grade and were used as commercially supplied. TLC analyses utilized glass-backed silica gel plates (E. Merck, 5715) and were visualized with anisaldehyde/acetic acid/ethanol stain or UV lamp. Standard gravity column chromatographic separations employed Kieselgel 60 (E. Merck, 7734, 70-230 mesh). Flash column chromatographic separations[22] utilized Kieselgel 60 (E. Merck, 9385, 230–400 mesh), and Celite filtrations were done with Johns-Manville Celite 521. Filtrates and chromatographic fractions were concentrated under vacuum at room temperature using a standard rotary evaporator. Vacuum Kugelrohr distillations were run with a Büchi oven. Ultrasound was generated with a Sonics and Materials Model VC 300 power supply tuned to 20 kHz and fitted with titanium and stainless steel probes.

Preparation of Chromyl Chloride (1). (i) Without Ultrasound. Commercial-grade CrO_3 (3.22 g, 32.2 mmol)[23] was ground to a fine powder and transferred to a round-bottomed flask containing freshly distilled CH_2Cl_2 (80 mL) and equipped with a magnetic stirring bar, septum, and argon inlet. Commercial-grade $TiCl_4$ (3.05 g, 16.1 mmol) was then added by syringe (rt) while stirring whereupon the red-brown suspension slowly changed to a light red solution and TiO_2 began to precipitate. Stirring was continued (8–12 h) after which the reaction solution was cherry red in color and the white precipitate of TiO_2 was sufficiently preponderant to slow the stirring process. An aliquot was taken from the reaction mixture, and the CH_2Cl_2 was then removed by fractional distillation (atmospheric pressure) followed by distillation of the product: bp 117 °C (760 mmHg) [lit.[24] bp 122 °C (760 mmHg)]. **(ii) Ultrasound-Promoted.** Commercial-grade CrO_3 (3.22 g, 32.2 mmol) was ground to a fine powder and transferred to a jacketed reaction flask (250 mL) containing freshly distilled CH_2Cl_2 (80 mL) which was cooled (20 °C) with a constant-temperature circulating bath (ethylene glycol/water (50/50)). Commercial-grade $TiCl_4$ (3.05 g, 16.1 mmol) was added as above, and the ultrasound probe was immersed in the reaction mixture and activated (high intensity). After 2.5 h the sonication was stopped and the cherry red solution was used directly for all the described transformations. The distilled yield (117 °C (760 mmHg)) of pure chromyl chloride prepared by ultrasound was 70%.

General Procedure for the Preparation of Chromate Ester Oxidants 2 and 3. The alcohol 4 or 5 (2.03 mmol) was dissolved in CH_2Cl_2 (10 mL) and added to a round-bottomed flask fitted with a dropping funnel and containing anhydrous K_2CO_3 (6.09 mmol) and a stir bar. The dropping funnel was charged with CrO_2Cl_2 (2.0 mmol) in CH_2Cl_2 (30 mL) and added dropwise to the solution of the diol or alcohol while being stirred and cooled (−78 °C). After the addition of the CrO_2Cl_2 was complete (1 h) the reaction mixture was allowed to warm (rt), resulting in an orange-red solution which was used directly in the oxidations of the alcohol substrates.

General Procedure for the Oxidation of Alcohols to the Corresponding Carbonyl Compounds Using the Chromate Ester Oxidants 2 and 3. Table I. The freshly prepared solution of either of the chromate ester oxidants 2 or 3 as prepared above was stirred at rt as a solution of the substrate alcohol (1.0 mmol) in CH_2Cl_2 (1 mL) was added. After the reaction was complete (1 h) as indicated by TLC analysis, the reaction mixture was vacuum-filtered with a fritted glass funnel packed with silica gel (70–240 mesh, 12 g) on top of Celite 521 (4 g), and the residue and filter adsorbents were washed with ethyl acetate (220 mL) and ether (2 × 20 mL). The filtrate was concentrated, and the product was purified by column chromatography or Kugelrohr distillation.

Acetophenone (entry 1, Table I): purified (>99%, TLC) by silica gel column chromatography (9:1 pentane/EtOAc) and Kugelrohr-distilled, bp 82–85 °C (1 mm) [lit.[25] bp 201 °C (736 mm)].

Benzophenone (entry 2, Table I): purified (>99%, TLC) by silica gel column chromatography (15:1 pentane/EtOAc), mp 161–162 °C [lit.[26] mp 160–161 °C].

***p*-Nitrobenzaldehyde (entry 3, Table I):** purified (>99%, TLC) by silica gel column chromatography (15:1 pentane/EtOAc) and Kugelrohr-distilled, mp 105–106 °C (lit.[27] mp 106–106.5 °C).

2-Octanone (entry 4, Table I): purified (>99%, TLC; 15:1 pentane/EtOAc) by Kugelrohr distillation, bp 50–52 °C (1 mm) [lit.[28] bp 170–172 °C (760 mm)].

4-*tert*-Butylcyclohexanone (entry 5, Table I): purified (>99%, TLC) by silica gel column chromatography (3:1 hexanes/EtOAc), mp 49–50 °C [lit.[29] mp 49–50 °C].

4-Phenylcyclohexanone (entry 6, Table I): purified (>99%, TLC) by silica gel column chromatography (9:1 pentane/EtOAc), mp 78–80 °C (lit.[30] mp 78 °C).

Étard Oxidation of Diphenylmethane (entry 1, Table II). (i) Ultrasound-Promoted. A solution of diphenylmethane (0.10 g, 0.59 mmol) in CH_2Cl_2 (10 mL) was added dropwise to a cooled (0 °C) solution of freshly prepared CrO_2Cl_2 (1.78 mmol) in CH_2Cl_2 (50 mL) while sonication took place (maximum intensity). After addition, sonication was continued and the reaction mixture was allowed to warm (~22 °C). Within 30 min the color of the reaction mixture changed from cherry-red to dark brown indicating the formation of the complex. Sonication was continued (0.5 h) followed by the addition of Zn dust (0.20 g, 3.1 mmol) and continuation of sonication (0.5 h, low intensity). The reaction mixture was cooled (0 °C), and ice (10 g) was added with continued sonication (0.5 h, maximum intensity). The green solution was poured into a separatory funnel, and the CH_2Cl_2 layer was separated. The aqueous layer was extracted with CH_2Cl_2 (3 × 20 mL), and the combined extracts were washed with brine (50 mL) and dried (Na_2SO_4). The drying agent was removed by vacuum filtration, and the filtrate was concentrated to provide a colorless oil which was purified (>99%, TLC; 25:1 pentane/EtOAc) by silica gel column chromatography followed by Kugelrohr distillation [bp 130–135 °C (4 mmHg) (lit.[26] bp 187–190 °C (15 mmHg))]. **(ii) Without Ultrasound.** A solution of diphenylmethane (0.10 g, 0.59 mmol) in CH_2Cl_2 (10 mL) was added dropwise to a stirred solution (0 °C) of freshly prepared CrO_2Cl_2 (1.78 mmol) in CH_2Cl_2 (50 mL). The reaction mixture was allowed to warm (~22 °C, 1 h), and the color of the reaction mixture changed from cherry-red to dark brown indicating the formation of the complex. Stirring was continued (0.5 h) followed by the addition of Zn dust (0.20 g, 3.1 mmol). After 30 min the reaction mixture was cooled (0 °C) and ice (10 g) was added with continued stirring (0.5 h). Workup, purification, and properties were the same as in the above procedure.

Étard Oxidation of Triphenylmethane (Entry 2, Table II). (i) Ultrasound-Promoted. A solution of triphenylmethane (0.10 g, 0.41 mmol) in CCl_4 (10 mL) was added dropwise to a cooled (0 °C) solution of freshly prepared CrO_2Cl_2 (1.25 mmol)

(21) Suslick, K. S.; Schubert, P. F.; Goodale, J. W. *J. Am. Chem. Soc.* **1981**, *103*, 7342. Suslick, K. S.; Goodale, J. W.; Wang, H. H.; Schubert, P. F. *J. Am. Chem. Soc.* **1983**, *105*, 5871. Suslick, K. S.; Schubert, P. F. *J. Am. Chem. Soc.* **1983**, *105*, 5781. Suslick, K. S.; Gawienowski, J. W.; Schubert, P. F.; Wang, H. H. *J. Phys. Chem.* **1983**, *87*, 2299. Suslick, K. S. Homogeneous Sonochemistry. In *Ultrasound: Its Chemical, Physical and Biological Effects*; Suslick, K. S., Ed.; VCH: New York, 1988.

(22) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

(23) **Caution**: Handle all Cr(VI) reagents with care; the mutagenicity of Cr(VI) compounds is well documented: Wetterhahn, K. E.; Cupo, D. Y. *Cancer Res.* **1985**, *45*, 1146 and references cited therein.

(24) See ref 9b.

(25) Noller, C. R.; Adams, R. *J. Am. Chem. Soc.* **1924**, *46*, 1893.

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in CCl_4 (50 mL) while sonication took place (maximum intensity). After addition, the reaction mixture was allowed to warm (~22 °C). Within 25 min the color of the reaction mixture changed from cherry-red to dark brown indicating the formation of the complex. Sonication was continued (0.5 h) followed by the addition of Zn dust (0.20 g, 3.1 mmol) and sonication resumed (0.5 h, low intensity). Workup as in entry 1 provided a brownish white solid which was purified by silica gel column chromatography (>99%, TLC; 15:1 pentane/EtOAc) to yield a white powder (mp 161–162 °C (lit.[31] mp 160–162 °C)). **(ii) Without Ultrasound.** A solution of triphenylmethane (0.10 g, 0.41 mmol) in CCl_4 (10 mL) was added dropwise to a stirred solution (0 °C) of freshly prepared CrO_2Cl_2 (1.25 mmol) in CCl_4 (50 mL). The reaction mixture was allowed to warm (~22 °C, 1 h) whereupon the color of the reaction mixture changed from cherry-red to dark brown indicating the formation of the complex. Stirring was continued (0.5 h) followed by the addition of Zn dust (0.20 g, 3.1 mmol). After 30 min the reaction mixture was cooled (0 °C), and ice (10 g) was added with continued stirring (0.5 h). Workup, purification, and properties were the same as in the above procedure.

Étard Oxidation of Indan (Entry 3, Table II). (i) Ultrasound-Promoted. A solution of indan (0.10 g, 0.85 mmol) in CH_2Cl_2 (10 mL) was added dropwise to a cooled (0 °C) solution of freshly prepared CrO_2Cl_2 (2.53 mmol) in CH_2Cl_2 (50 mL) while sonication took place (maximum intensity). After the addition was complete, the reaction mixture was allowed to warm (~22 °C), and the color of the reaction mixture changed from cherry-red to dark brown. Sonication was continued (1 h) followed by the addition of Zn dust (0.41 g, 6.3 mmol), and sonication was resumed (0.5 h low intensity). Workup as in entry 1 provided a colorless oil. Purification by flash chromatography (>99%, TLC; 15:1 pentane/EtOAc) afforded 1-indanone as crystalline plates (mp 41–42 °C (lit.[32] mp 42 °C)). **(ii) Without Ultrasound.** A solution of indan (0.10 g, 0.85 mmol) in CH_2Cl_2 (10 mL) was added dropwise to a stirred solution (0 °C) of freshly prepared CrO_2Cl_2 (2.53 mmol) in CH_2Cl_2 (50 mL). The reaction mixture was allowed to warm (~22 °C, 15 min) during which time the color of the reaction mixture changed from cherry-red to dark brown. Stirring was continued (1 h) followed by the addition of Zn dust (0.41 g, 6.3 mmol). After 30 min the reaction mixture was cooled (0 °C), and ice (10 g) was added with continued stirring (0.5 h). Workup, purification, and properties were the same as in the above procedure.

Oxychlorination of *trans*-2-Octene (Entry 4, Table II). (i) Ultrasound-Promoted. A solution of *trans*-2-octene (0.10 g, 0.89 mmol) in acetone (7 mL) was added in one portion to a cooled (−78 °C) sonicated (high intensity) solution of freshly prepared CrO_2Cl_2 (1.87 mmol) in CH_2Cl_2 (10 mL), under Ar. During the addition the color changed from cherry-red to dark brown. Sonication was continued (1 h) followed by addition of 20% aqueous sodium bisulfite (5 mL). The reaction mixture was allowed to warm (rt) with continued sonication (0.5 h) which resulted in a green homogeneous solution. The reaction mixture was then diluted with CH_2Cl_2 (20 mL) and transferred to a separatory funnel. The CH_2Cl_2 layer was separated, and the aqueous layer was washed with CH_2Cl_2 (3 × 20 mL). The combined extracts were washed with brine and dried over Na_2SO_4. Removal of the drying agent and removal of the solvent resulted in a colorless oil which was flash chromatographed (4:1 pentane/Et_2O) and Kugelrohr distilled (bp 35–40 °C (4 mm)) to furnish a mixture of isomeric chloro ketones[33] as indicated by ^1H NMR analysis. **(ii) Without Ultrasound.** A solution of freshly prepared CrO_2Cl_2 (1.87 mmol) in CH_2Cl_2 (10 mL) was added dropwise to a stirred cooled (−78 °C) solution of *trans*-2-octene (0.10 g, 0.89 mmol) in acetone under Ar. During the addition the color of the reaction mixture changed from cherry-red to dark brown. The reaction mixture was stirred for 1 h. 20% aqueous solution of sodium bisulfite (5 mL) was added, and the mixture was allowed to warm (rt). Workup, purification, and properties were the same as in the above procedure.

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