tracted with diethyl ether (2 × 35 mL), acidified with dilute HNO_3, and titrated with 0.07 M $AgNO_3$.

In an experiment with **1a** and $Ph_2P^-K^+$ at initial concentrations of 0.04 and 0.2 M, respectively, bromide ion concentration was determined to be 0.091×10^{-3} M at 2.4 min, 0.203×10^{-3} M at 21.8 min, 0.378×10^{-3} M at 61.6 min, and 1.51×10^{-3} M at 372 min.

Reaction of Potassium Diethyl Phosphite with *p*-Iodotoluene in Dimethyl Sulfoxide in the Dark. The apparatus consisted of a 100-mL round-bottom flask with a gas inlet side arm, equipped with a short condenser topped with a ground glass stopper. The condenser and top half of the flask were wrapped in black plastic tape. The flask was flushed with argon and kept under a positive argon pressure. Me_2SO (50 mL), *t*-BuOK (1.34 g, 0.012 mol), and diethyl phosphonate (1.38 g, 0.01 mole) were added and stirred. The mixture was equilibrated in a 25 °C bath and *p*-iodotoluene (0.44 g, 0.002 mol) added. The mixture was stirred and returned to the water bath. Aliquots (5 mL) were withdrawn and added to 25 mL of water to quench the reaction. The samples were extracted with ether (3 × 25 mL), and the aqueous phase was titrated for iodide ion with 0.07 M $AgNO_3$.

Biphenyl was added to the ether extracts as an internal standard, and the amount of diethyl phenylphosphonate was determined by GLC (5% SE-30, 1.52 m × 3.2 mm, 135 °C).

In a second reaction, the procedure used was identical, but diphenylphosphine (0.1967 g, 0.00106 mol) was added with the diethyl phosphonate. The analysis was identical, but after the diethyl phenylphosphonate was determined the ether phase was oxidized as previously described and the amount of diphenyl-*p*-tolylphosphine oxide was determined by GLC with use of triphenylphosphine oxide as internal standard.

Entrainment of 1a by Addition of 1b, and 1b/1a Reactivity Ratio in Me_2SO. The initial concentrations were 0.04 M in **1a** and 0.20 M in $Ph_2P^-K^+$, and the general procedure described for rate measurements was followed. Aliquots taken at 3.7, 10.3, 19.9, and 42.0 min were analyzed for Br^- by potentiometric titration with $AgNO_3$. At 42.6 min, 0.2 mL of a 2 M solution of **1b** in Me_2SO was added (to achieve a **1b** concentration of 0.0133 M), and subsequent aliquots were analyzed with observation of both the I^- and the Br^- end points. The amount of bromide ion released is plotted in Figure 3; the amount of iodide ion released was about 13 times the increment of bromide ion release after addition of **1b**. By means of eq 5, the reactivity ratio, k_{1b}/k_{1a}, was reckoned to be 240 at 43.2 min, 130 at 44.0 min, 140 at 44.6 min, 150 at 55.2 min, and 120 at 70.3 min. In a similar experiment with result like that shown in Figure 3, **1b** to 0.016 M was added at 63.2 min, and k_{1b}/k_{1a} was reckoned as 110 at 64.0 and 130 at 64.8 min.

Effects of Additives on Reactions of 1b in Me_2SO. Initial concentrations were 0.04 M for **1b** and 0.20 M for $Ph_2P^-K^+$, and the general procedure described for rate measurements was followed. The results for reaction with no additive, with 0.0083 M *m*-dinitrobenzene, with 0.0081 M azobenzene, and with 0.0080 M di-*tert*-butyl nitroxide are plotted in Figure 2. Another experiment (not plotted) with 0.0084 M *m*-dinitrobenzene showed much stronger deceleration, to about three-fifths the amount of reaction shown in Figure 2 for aliquots within the first 3 min. With 0.0042 M 1,1-diphenylethene or 0.0086 M *p*-dinitrobenzene, iodide ion release within the first 2 min was nearly as great as in the absence of additives.

Registry No.—**3,** 1031-93-2; **5,** 6840-28-4; **6,** 6840-27-3; potassium diphenylphosphide, 15475-27-1; diphenylphosphine, 829-85-6.

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Mechanism of the α-Chlorination of Propylbenzene by Chromyl Chloride

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Optically active α-deuteriopropylbenzene has been treated with chromyl chloride and gives optically active 1-chloro-1-phenylpropane in 35–40% yield. This reaction proceeds with net overall retention of configuration (about 35%) accompanied by considerable racemization (65%), even at early reaction times. Product chloride itself racemizes during the reaction as well. A radical pair mechanism is supported by the data.

We wish to report the results of our study of the α-chlorination of propylbenzene (1) by chromyl chloride. These results support a radical pair mechanism for the chlorination and are not consistent with concerted or radical chain formulations of this reaction.

$$C_6H_5CH_2CH_2CH_3 + CrO_2Cl_2 \rightarrow C_6H_5CH(Cl)CH_2CH_3$$
$$\mathbf{1} \qquad\qquad \mathbf{2}$$

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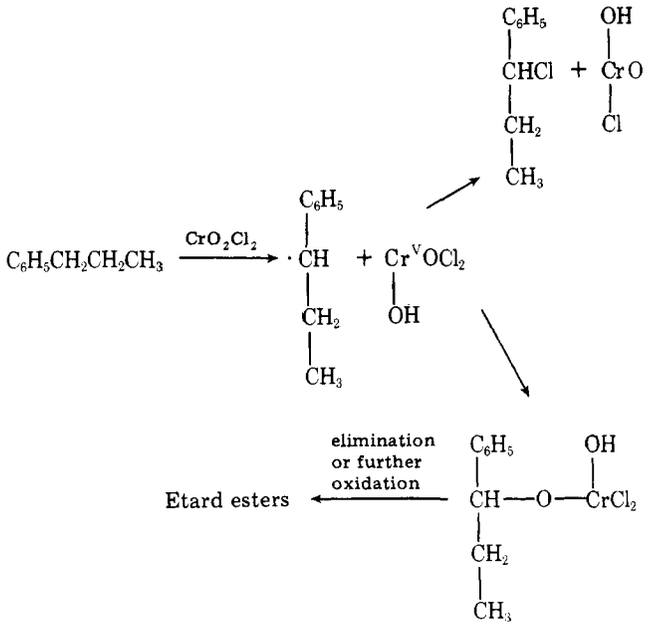
Chromyl chloride is a powerful oxidant, and in solutions of CCl_4 or CS_2 it provides a satisfactory means of converting alkylbenzenes into various products of side chain oxidation.[1] For example, reaction of toluene derivatives with chromyl chloride provides insoluble Étard esters which can be hydrolyzed in moderate yields to aldehydes (the Étard reaction).[2]

$$ArCH_3 + CrO_2Cl_2 \xrightarrow{CCl_4} [ArCH_3 \cdot 2CrO_2Cl_2] \xrightarrow{H_2O} ArCHO$$

Reaction of longer chain alkylbenzenes with chromyl chloride gives more complex reaction mixtures. The oxidation of propylbenzene, studied in detail by Wiberg, Marshall, and Foster,[3] gave a mixture of products (eq 1), with ratios de-

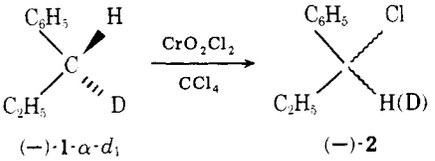
$$C_6H_5CH_2CH_2CH_3 \xrightarrow[CCl_4]{CrO_2Cl_2} C_6H_5CH(Cl)CH_2CH_3 + C_6H_5C(=O)CH_2CH_3 + C_6H_5CH_2C(=O)CH_3 \quad (1)$$

pendent on CrO_2Cl_2 concentration. Wiberg, Marshall, and Foster[3] proposed a radical pair mechanism, beginning with formation of a benzylic radical and a Cr^V species, a pair which



was postulated to collapse to a chromium ester or to disproportionate to an α-chlorinated product and a chromium(IV) species. This scheme is thus analogous to other proposals for permanganate[4] and chromic acid[5] C–H activation. However, as pointed out by Wiberg,[5b] these results did not allow one to eliminate completely concerted mechanisms or radical chain formulations of this reaction.

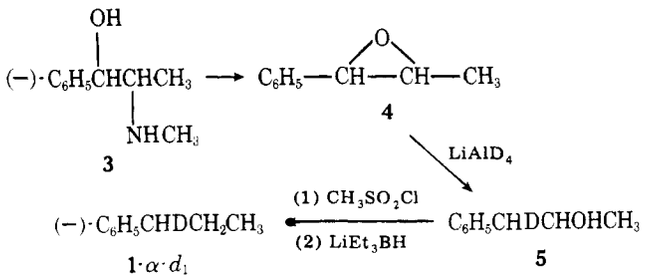
We have studied this reaction by examining the stereochemistry of the chromyl chloride chlorination of α-deuteriopropylbenzene,[6] (−)-1-α-d_1. This system should be capable,



(−)-1-α-d_1 (−)-2

in principle, of distinguishing three limiting mechanisms. (a) If the reaction is concerted, one would anticipate that each enantiomer would contain only H or D (depending on whether the reaction occurred with overall retention or inversion). (b) If radical chain processes are involved, then all products, whether H- or D-containing, should be racemic because of the intervention of the kinetically free, planar benzylic radical.

Scheme I



(c) If a radical pair formulation is accurate, then incomplete but significant retention of configuration might be expected in line with other observations, particularly in permanganate oxidation of tertiary C–H centers.

Preparation of Starting Material and Optical Correlation of the Product. The preparation of optically active α-deuteriopropylbenzene is shown in Scheme I. The chiral compound (*R*)-(−)-1-α-d_1 was prepared in three steps from *trans*-β-methylstyrene oxide (**4**), which was, in turn, prepared from (−)-ephedrine (**3**) according to the method of Fischer.[7] The epoxide was treated with $LiAlD_4$ in ether at reflux for 6 h. Base workup gave 70–80% of the anticipated alcohol (**5**). Chiral undeuteriated alcohol **5** has been assigned the configuration *R*-(−), $[\alpha]^{20}_D$ 16.13° (EtOH).[9] Our deuteriated material had $[\alpha]^{20}_D$ −17.47°. NMR analysis of the MTPA ester[8] of this alcohol confirmed that the material was *enantiomerically* pure at the carbinol carbon. Conversion of **5** to **1** was accomplished by treatment of the mesylate corresponding to **5** with $LiEt_3BH$ in THF, yield 75%. The resulting deuteriopropylbenzene was shown to be cleanly monodeuteriated by NMR and had $[\alpha]^{20}_D$ −1.13 (neat) and −1.40° (CCl_4). We assume that the ring opening of the epoxide proceeded with clean inversion of stereochemistry at C_1 and infer that the 1-deuterio-1-phenylpropane is *R* as shown.

Although the product of the reaction under study, optically active 1-chloro-1-phenylpropane, has been described several times in the literature, only limiting values for its optical purity, based on the purity of starting materials, have been available. In a typical study, Kwart and Hoster[10] reported the results shown in eq 2, but in general no assurance is available on the optical integrity of the $SOCl_2$ reaction.[11]

$C_6H_5CH(OH)CH_2CH_3$
6, $[\alpha]^{25}_D$ −24.30° (neat)

$$\xrightarrow{SOCl_2} \underset{\textbf{2},\ [\alpha]^{25}_D\ -37.2°\ (\text{acetone})}{C_6H_5CH(Cl)CH_2CH_3} \quad (2)$$

We were able to obtain an accurate measure of the optical rotation/enantiomeric excess correlation for this chloride employing the method shown in Scheme II and Table I. Since

Scheme II

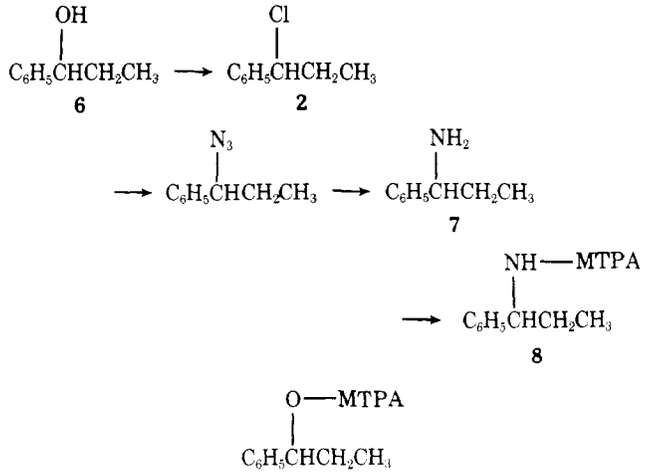


Table I

expt	ROH [α],[11] deg	ROH, % ee	RCl [α],[11] deg	RNH_2, % ee	calcd [α] for pure RCl in CCl_4, deg
(1) 50% conv RCl → RN_3	+11.4 (neat)	48	+21.3 (acetone) +22.5 (CCl_4)	14	160
(2) 100% conv RCl → RN_3		same		18	125
(3) 50% conv RCl → RN_3	not measd	90	−55.0 (CCl_4)	54	102
(4) 100% conv RCl → RN_3		same		50	110

Table II

time, h	0	0.5	1.0	2.11	3.5	5
α-propylbenzene-d_1	4.1	3.48	3.11	2.48	2.25	1.98
α-chloropropylbenzene	0	0.15	0.27	0.52	0.69	0.83
rotation of α-chloropropylbenzene, $[\alpha]^{20}_D$		−28°	−18.5°	−8.2°	−4.5°	−3.6°

the enantiomeric excess of amine **7** can be determined accurately by conversion to MTPA amide[8] **8**, it follows that the ee of optically active chloride **2** can be determined if the displacement by azide ion (**2** → azide) is well behaved. That this is so can be demonstrated by interrupting the azide displacement at partial and complete conversion and showing that the derived amine is chiroptically identical under both conditions. These data are shown in Table I. Thus, optically pure chloride has a rotation in excess of 100°. Since experiments 3 and 4 involve higher enantiomeric ratios, which represent inherently more accurate measurements by the NMR method, these values probably represent the more accurate experiments in our system. We assign to $[\alpha]^{25}_D$ (CCl_4) a value of 106°. It is interesting to note that in our conversion of alcohol to chloride by the thionyl chloride method, considerable loss of optical purity is involved.[11]

Reaction of Deuteriated Hydrocarbon with Chromyl Chloride. Treatment of 0.2–0.4 M solutions of **1** with slight molar excesses of CrO_2Cl_2 in CCl_4 followed by filtration and washing of the filtrate gave **2**. As noted by others,[5b] the chloride **2**, starting material, and CrO_2Cl_2 are virtually the only materials found in filtered reaction mixtures.

The yield of **2** is constant at about 35 ± 5% (based on consumed starting material). With excess chromyl chloride, **2** also begins to disappear at long reaction times (>5 h).

Chloride **2** isolated after nearly complete disappearance of starting material (12 h) showed a barely visible NMR signal due to benzylic protons. Thus, the isotope effect for this reaction is very high, k_H/k_D = 10–20, similar to high isotope effects ($k_H/k_D \sim 12$) found for permanganate and chromate oxidations of C–H bonds.[4,5]

Chloride isolated after a reaction of chiral **1** for 4–6 h was distinctly levorotatory. Since this chloride is known to be *S*-(−), the reaction from *R*-(−) hydrocarbon is clearly occurring with retention of configuration (see Scheme I).

Material isolated after reaction overnight is virtually racemic. Since it was clear that **2** was racemizing under the reaction conditions, attempts were made to determine the optical rotation of the chloride as a function of time. The result of measuring $[\alpha]^{20}_D$ for product chloride as a function of time is given in the Experimental Section. From these data, it is obvious that $[\alpha]^{20}_D$ at time = 0 will be much greater than [α] (0.5 h) −28°.

Analytical difficulties prevented us from obtaining [α] measurements on product chloride at times much shorter than 0.5 h. Even at this point, however, the enantiomeric excess is >25%, and the extrapolation to higher values, possibly 35–40% ee, seems clear.

The origin of the product racemization is unclear. The process could be due either to chloride displacement of Cl^- (from HCl produced in the reaction) or from an ionization of the benzylic chloride assisted by chromyl chloride acting as a Lewis acid. Further work would be needed to clarify this point.

Discussion

Other high valent oxotransition metal species are also capable of functionalizing C–H units.[2–5] In particular, MnO_4^- and CrO_4^{2-} have been investigated extensively in aqueous solution. Complete mechanistic studies seem to agree[5b] that in these systems the dominant mechanism must be hydrogen atom abstraction (i.e., one-electron step) followed by a significant degree of cage recombination. Again in these aqueous systems the oxidation of chiral tertiary centers always leads to *retention* of configuration with enantiomer excesses generally of 30–40%.

In the oxidation of propylbenzene by chromyl chloride, the stereochemical evidence presented in this study together with the earlier product and kinetic analyses of Wiberg strongly suggest that chromyl chloride in CCl_4 behaves as a typical Cr(VI) or Mn(VII) species. The present experiment is amenable to two interpretations. One would involve a high degree of cage recombination, with recombination competing with rotation of the benzyl radical. A second distinct possibility would be a cage recombination with a high degree of stereochemical retention mixed with a noncage process leading to a racemic product. Indeed this latter possibility seems to be clearly implicated in the thermal Meisenheimer rearrangement of benzylmethylphenylamine *N*-oxide studied by Schollkopf[15] and Lorand.[16]

In either event, the present experiment allows for a significant degree of radical involvement in the chlorination. Although perhaps surprising, it appears that no new mechanistic pathways open up even though this reagent has the added possibility of transferring a chlorine atom and the advantage of operating in a nonsolvating medium.

Experimental Section

General. NMR spectra were obtained at 60 MHz using either a T-60 or an A-60 Varian spectrometer. Optical rotations were obtained in a 1-dm H_2O-jacketed cell (20 °C) using a Perkin-Elmer Model 141 spectropolarimeter.

(+)-*trans*-β-Methylstyrene Oxide (4). This material was prepared following the procedure of Fischer[7] to give material with $[\alpha]^{20}_D$ 77° (CH_2Cl_2) [lit. $[\alpha]_D$ 70.5° (neat)].

(−)-(1*R*,2*R*)-1-Deuterio-2-hydroxy-1-phenylpropane (5). Lithium aluminum deuteride (Stohler), 230 mg, was stirred in 20 mL of dry ether, and 1.5 g of **4** was added in 5 mL of ether dropwise. This mixture was refluxed for 6 h and then worked up in the usual manner with NaOH solution, yield 1.0 g (66%).

Mesylate of Compound 5. This mesylate was prepared in high yield by the method of Crossland and Servis.[14] This product was not

separately isolated, but did show the clean NMR spectrum characteristic of these reactions.

Preparation of 1-α-d_1. The reduction of the mesylate was best accomplished with $LiEt_3BH$ in THF (Aldrich "Superhydride"). Thus, 45 mL of 1 M $LiEt_3BH$ in THF was added to 7.3 g of the mesylate of **5** (above). This mixture was refluxed overnight and then partitioned between pentane and water. Removal of pentane revealed substantial amounts of ethyl-containing impurities, presumably Et_3B, which were removed by treatment with NaOH solution (10%) for a short time. Repartitioning between pentane and water followed by distillation gave 2.1 g of propylbenzene, 99% pure by VPC analysis. NMR analysis showed clean monodeuteration, 0.97 ± 0.05 d_1 by multiple integration. The rotations were $[\alpha]^{20}_D$ −1.13 (neat) and 1.40° (10% CCl_4 solution).

Reaction with Chromyl Chloride. In general, chromyl chloride was added by microliter syringe to a 5–10% solution of propylbenzene in CCl_4 containing hexachloroethane as an internal standard for VPC analysis. Slightly greater than molar ratios of CrO_2Cl_2 were employed in runs reported here. Higher amounts of CrO_2Cl_2 resulted in diminished yields of chlorinated product. Reactions were run for the times indicated in Table II at ice-bath temperatures. The data presented represent millimoles of material as measured by VPC. Rotations of the α-chlorinated product are also shown.

Determination of Optical Purity of Chloride. The resolution of 1-phenyl-1-propanol and its conversion to chloride followed the procedures of Kwart and Hoster.[10] Chlorides of various optical rotations (see Table I) were then treated with a 5-fold excess of NaH_3 in DMF at room temperature. The half-life of this reaction was about 7 h, and complete reaction occurred in about 24 h. About half of these reaction mixtures were worked up after 5–6 h by pouring into water and extracting with ether.

This ether solution of azide and alcohol was then dried ($MgSO_4$) and treated with lithium aluminum hydride at room temperature for 2 h. Base workup (NaOH) gave an ether solution of amine and alcohol which was separated by normal acid wash/neutralization/ether extraction procedures. Preparation of the MTPA esters and amides allowed the optical purity to be determined.

MTPA esters and amides were prepared as described by Dale, Dull, and Mosher.[8] Analyses were accomplished by ^{19}F NMR using a Varian A56-60 spectrometer.

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Registry No.—1-α-d_1, 68408-59-3; **2**, 10316-10-6; **4**, 13595-05-6; **5**, 68473-92-7; **5** mesylate, 68408-60-6; chromyl chloride, 14977-61-8.

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Reductive Acetoxylation on α,α'-Dibromocycloalkanones by Ultrasonically Dispersed Mercury

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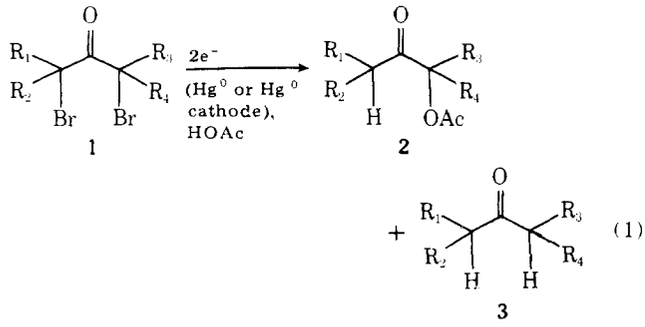
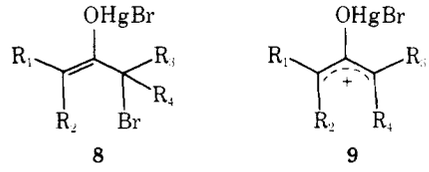
The α,α'-dibromocycloalkanones of ring size 5–12 were reduced by ultrasonically dispersed mercury in acetic acid. Products were the corresponding cycloalkanone and α-acetoxycycloalkanone. The ratio of these two is quite sensitive to ring size, and this fact is used to support the intermediate formation of 2-hydroxyallyl cations as precursors of the keto acetates. Molecular mechanics calculations support the proposed mechanism.

We[2,3] and others[4] have reported the electrochemical reductive acetoxylation of α,α'-dibromo ketones (**1** → **2**) in acetic acid. More recently, we discovered a similar conversion effected by ultrasonically dispersed metallic mercury.[5] In both reactions the reductive substitution product (**2**) is accompanied by the double reduction product **3** (or "parent" ketone, so-called because **1** is prepared from **3**) (eq 1). Small amounts of side products (most commonly α-bromo ketones or α,β-unsaturated ketones) often accompany **2** and **3**, but usually **2** and **3** constitute >90% of the reaction products, which are formed in high (85–94%) absolute yields in the electrochemical reaction but lower yields (30–75%) in the mercury reaction (the lower yields in the latter case possibly arising from partial conversion of **1** to insoluble organomercury byproducts).[5] We have advanced[2,3] the mechanism shown in Scheme I to ac-



1 2 3 (1)



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