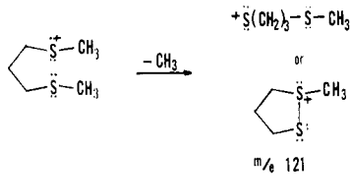
Scheme IV. Cleavage of 2,6-Dithiaheptane



in 1,4-dithiacyclooctane and at *m/e* 60 in 1,4-dithiane are most likely due to fragments in this series rather than to the dications. To further support the belief that no dicationic species are formed in any of these dithioethers, it is noted that there is *no peak* at *m/e* 81 in the spectrum of 1,5-dithiacyclononane or 1,4-dithiacyclononane or at *m/e* 67 in 1,4-dithiacycloheptane.

The mass spectra of some acyclic dithioethers were obtained by Shuttleworth,[6] who reported relatively intense peaks at *m/e* 121 in 2,6-dithiaheptane (Scheme IV) and *m/e* 135 in 2,7-dithiaoctane corresponding to loss of a CH_3 group from the cation radical. However, the intensity of the peaks at *m/e* 107 in 2,5-dithiahexane and at *m/e* 149 in 2,8-dithianonane, which are attributed to the loss of one CH_3 group from the parent, were lower. Budzikewicz, Djerassi, and Williams[2] suggested that the *m/e* 121 peak in 2,6-dithiaheptane might be due to a cyclic ion rather than to a linear ion. In view of our results on mesocyclic dithioethers, the formation of cyclic ions in 2,6-dithiaheptane and 2,7-dithiaoctane appears more plausible. Since we did not observe either four-membered or seven-membered ring formation in mesocyclic systems in which two thioether sulfurs were bridged by two and five methylene groups, the rather low intensity of the peaks at *m/e* 107 and 149 in the mass spectrum of 2,5-dithiahexane and 2,8-dithianonane, respectively, are expected.

Experimental Section

The mass spectra were run on a CE 21-104. The 1,4-dithiane was purchased from the Aldrich Chemical Co., Inc., and was sublimed before use. 1,4-Dithiacycloheptane,[7] 1,5-dithiacyclooctane,[8] 1,4-dithiacyclooctane,[9] 1,5-dithiacyclononane,[9] 1,6-dithiacyclodecane,[10] 2,5-dithiahexane,[11] 2,6-dithiaheptane,[12] and 2,7-dithiaoctane[12] were synthesized following reported procedures.

1,4-Dithiacyclononane. Into a 3-neck 2-L Morton flask fitted with overhead stirrer, condenser, and adaptor for syringe pump was added 1 L of absolute ethanol. With stirring, 12 g (0.52 g-atom) of freshly cut sodium was added under nitrogen. The solution was heated to 50 °C and 21 mL (0.25 mol) of 1,2-ethanedithiol diluted to 100 mL with absolute ethanol and 57.5 g (0.25 mol) of 1,5-dibromopentane diluted to 100 mL with absolute ethanol were added simultaneously by a syringe pump at a rate of 0.30 mL/min. The mixture was refluxed for 0.5 h and then concentrated under vacuum. Water was added to the remaining thick oil, and the mixture was extracted three times with dichloromethane. The combined organic phase was dried over Na_2SO_4, filtered, and concentrated under vacuum. The residue was distilled under vacuum to give 0.24 g (0.6%) of 1,4-dithiacyclononane: bp 65–67 °C (0.3 mm); mp 59–60 °C; ^1H NMR (CCl_4) δ 2.8 (m, 8, CH_2-S), 1.9 (m, 6, —CH_2—); ^{13}C NMR ($CDCl_3$) δ 34.8, 33.5, 27.9, 24.5.

Registry No.—1,4-DT, 505-29-3; 1,4-DTCH, 6008-55-5; 1,5-DTCO, 6572-95-8; 1,4-DTCO, 6572-94-7; 1,5-DTCN, 6573-47-3; 1,6-DTCD, 51472-64-1; 2,5-DTH, 6628-18-8; 2,6-DTHP, 24949-35-7; 2,7-DTO, 15394-33-9; 2,8-DTN, 54410-63-8; 1,2-dithiolane cation radical, 66609-63-0; 1,2-dithiane cation radical, 56587-33-8.

Supplementary Material Available: Bar graphs showing the mass spectra of all the dithioethers are presented (5 pages). Ordering information is given on any current masthead page.

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Mechanism of Oxidation of Alkylaromatic Compounds by Metal Ions. 4. Cerium(IV) Pyridinium Chloride. A Novel Reagent for Side-Chain Oxidation of Highly Substituted Methylbenzenes[1]

Silvana Maini and Luigi Mandolini*

Centro C.N.R. di Studio sui Meccanismi di Reazione, Istituto di Chimica Organica, Università di Roma, 00185 Roma, Italy

Cesare Rol

Dipartimento di Chimica, Università, 06100 Perugia, Italy

Received November 14, 1977

Several reports on oxidation reactions of methylbenzenes by Ce(IV) compounds are available in the recent literature.[2] We have shown that ceric ammonium nitrate (CAN) in oxygen-free AcOH leads to a mixture of side-chain acetoxylated and nitrooxylated products.[2] In view of the general interest of reactions leading to side-chain functionalization of alkyl aromatic compounds, we have investigated the behavior of a different oxidizing system, namely ceric pyridinium chloride $(C_5H_6N)_2CeCl_6$ (referred to as CPC), in either MeOH or EtOH solution. We now wish to report on a product study of the oxidation by this reagent of some highly substituted methylbenzenes, namely, hexamethylbenzene (HMB), durene (DUR), and mesitylene (MES).

The oxidation reactions were carried out under reflux in a nitrogen atmosphere with 2 mol of oxidant per mol of hydrocarbon. The results (Table I) show that with either HMB or DUR fair to good yields of side-chain chlorinated and/or alkoxylated products are formed. In contrast, MES does not seem to be reactive enough as to compete with the "spontaneous" reduction of CPC in boiling MeOH.[3] Because of its low reactivity, the oxidation of MES in EtOH solution was not attempted. Interestingly, both the oxidation reaction and the "spontaneous" reduction of CPC are at least two orders of magnitude faster in MeOH than in EtOH. This phenomenon might be related to different structures of the dissolved Ce(IV) species in the two solvents, possibly due to varying extents of displacement of loosely bound chloro ligands by solvent molecules (vide infra).

A dramatic change in the reaction mixture composition was observed when oxygen was bubbled through the solution during the oxidation of DUR in MeOH. 2,4,5-Trimethylbenzaldehyde, mp 38.5–40 °C,[4] was isolated in 65% yield. It was in fact detected in the ^1H-NMR spectrum of the crude reaction product mostly as its dimethyl acetal **3**.[5] The latter was also

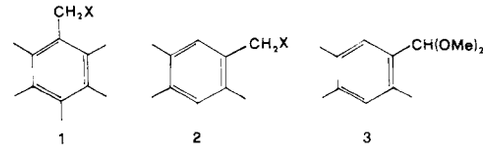

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Table I. Products Obtained in the Reaction of Some Methylbenzenes with CPC (1:2 mol ratio)

Substrate	Registry no.	Solvent	Time, h[a]	Products(s) (isolated yield, %)[b,n]
HMB	87-85-4	MeOH	ca. 0.05[c]	**1**, X = Cl (36);[d] X = OMe (38)[e]
DUR	95-93-2	MeOH	0.5	**2**,[f] X = Cl (35);[g] X = OMe (40)[h]
MES	108-67-8	MeOH	1.5	None
HMB		EtOH	3	**1**, X = OEt (75)[i]
DUR		EtOH	48[l]	**2**, X = OEt (47)[m]

[a] Time required at reflux temperature for a complete reduction of Ce(IV) to Ce(III), unless otherwise stated. [b] As based on starting hydrocarbon. Varying amounts of the latter were recovered in all cases thus leading to a nearly quantitative material balance. [c] The reaction was apparently controlled by the dissolution of HMB, which is sparingly soluble in MeOH at room temperature. [d] Mp 81–82 °C. See H. Hart and J. L. Relly, *Tetrahedron Lett.*, 143 (1977). [e] Mp 58–60 °C; ^{1}H NMR (CCl_4) δ 4.3 (s, 2 H, CH_2O), 3.2 (s, 3 H, OCH_3), 2.0–2.3 (m, 15 H, $ArCH_3$). [f] The absence of both chlorodurene and methoxydurene was checked by GLC analysis of the crude material (comparison with authentic samples). [g] ^{1}H NMR (CCl_4) singlets at δ 7.0 (1 H, ArH), 6.9 (1 H, ArH), 4.5 (2 H, CH_2Cl), 2.35 (3 H, $ArCH_3$), 2.2 (6 H, $ArCH_3$). [h] ^{1}H NMR (CCl_4) singlets at δ 6.9 (1 H, ArH), 6.75 (1 H, ArH), 4.3 (2 H, CH_2O), 3.2 (3 H, OCH_3), 2.15 (broad, 9 H, $ArCH_3$). [i] Bp 114 °C (0.6 mmHg), mp 28 °C. See I. I. Lapkin and R. C. Mukhina, *Zh. Obshch. Khim.*, **31**, 4001 (1961); *Chem. Abstr.*, **57**, 9710a. [l] Reduction of Ce(IV) was not complete. [m] The ^{1}H-NMR spectrum (CCl_4) was similar to that of **2**, X = OCH_3, with the sole difference that the OCH_3 signal was replaced by that of OCH_2CH_3. [n] Registry No.—**1** (X = Cl), 484-65-1; **1** (X = OMe), 20145-50-0; **2** (X = Cl), 10340-77-9; **2** (X = OMe), 18237-72-4; **1** (X = OEt), 65915-91-5; **2** (X = OEt), 65915-92-6.

formed besides **2**, X = Cl and OMe, in runs where nitrogen was either contaminated or omitted.

The oxidation of either HMB or DUR with CPC is characterized by a remarkable specificity. Exclusion of oxygen allows selective oxidation to the alcohol level. Furthermore, only one out of the several methyl groups is attacked, and no nuclear substitution occurs when nuclear positions are available. The reaction is of synthetic value, in that it allows side-chain methoxylation and ethoxylation in fair to good yields by means of a simple one-step procedure. In the former case a prolonged boiling of the reaction mixture is required after the reduction of CPC is complete, in order to solvolyze any chloromethyl derivative. In EtOH solution, the reaction time is such as to allow complete solvolysis of any side-chain chlorinated material possibly formed.

In order to check whether all the methyl ether was produced by methanolysis of the corresponding chloride, the side-chain methoxylation to chlorination ratio was determined at the very early stages of the oxidation reaction of DUR. The experiment was carried out at room temperature for experimental convenience, since at this temperature methanolysis of **2**, X = Cl, was slow (ca. 5% reaction after 90 min). Samples of the reaction mixture were taken at intervals, quenched with Fe^{2+}/MeOH, worked-up, and analyzed by GLC (Figure 1). Thus, a significant fraction, namely 0.25 of the oxidation reaction, led to direct side-chain methoxylation. The extent of side-chain methoxylation was reduced, although not completely suppressed, by addition of a large excess of LiCl.

The oxidation of polymethylbenzenes by CPC in MeOH bears striking similarities with the oxidation by CAN in AcOH, not only with respect to reaction products[1] either in the absence or in the presence of oxygen, but also to substrate selectivity leading in both reactions to the reactivity order HMB ≫ DUR ≫ MES.[6] The last point is noteworthy, since the observed pattern is inconsistent with a free-radical attack on the benzylic CH bond, for which a low substrate selectivity should be expected,[7] as well as with an electrophilic attack of molecular chlorine, possibly formed by oxidation of chloride ions by Ce(IV),[8] for which the reactivity order MES ≫ DUR is expected.[9] The intervention of molecular chlorine is further ruled out by the absence of chlorodurene in the reaction products. Rather, it seems more likely that CPC reacts via an electron-transfer mechanism (eq 1) as suggested for the reaction with CAN in AcOH,[1,6] for which the high substrate selectivity observed was related to the donor abilities of the hydrocarbons, as measured by the transition energies $h\nu_{CT}$ of their charge-transfer complexes with tetracyanoethylene.[6]

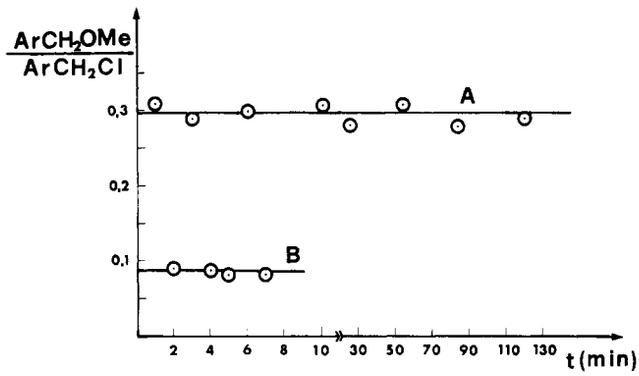

Figure 1. Side-chain methoxylation to side-chain chlorination molar ratio as a function of time for the reaction of DUR (0.03 M) with CPC (0.03 M) in MeOH at 19 °C (curve A). Curve B with added 1 M LiCl.

$$ArCH_3 + Ce(IV) \rightleftarrows ArCH_3^{+}\cdot + Ce(III) \quad (1a)$$

$$ArCH_3^{+}\cdot \rightarrow ArCH_2\cdot + H^+ \quad (1b)$$

$$ArCH_2\cdot + Ce(IV) \rightarrow \text{products} \quad (1c)$$

As to the mechanism for the conversion of the benzyl radicals to products, some information can be obtained from the data reported in Figure 1. A stepwise mechanism (eq 2), ac-

$$ArCH_2\cdot \xrightarrow{Ce(IV)} ArCH_2^{+} \begin{cases} \xrightarrow{Cl^-} ArCH_2Cl \\ \xrightarrow{MeOH} ArCH_2OMe \end{cases} \quad (2)$$

cording to which Ce(IV) oxidizes $ArCH_2\cdot$ to $ArCH_2^+$, which in turn is diverted into products by a competition between the solvent and free-chloride ions, seems unlikely in view of the fact that (i) the ratio of methoxylation to chlorination is remarkably constant with time and (ii) the large amount of added Cl^- ions, actually much greater than any amount possibly present at the early stages of the reaction, does not completely suppress the formation of the methoxy derivative. Rather, a ligand transfer mechanism[1,10] (eq 3) seems to ra-

$$ArCH_2\cdot + Ce^{IV}(Cl)_x(OMe)_y \rightarrow \begin{cases} ArCH_2Cl \\ ArCH_2OMe \end{cases} \quad (3)$$

tionalize the results better. This hypothesis requires that, in addition to chloro ligands, Ce(IV) possesses some methoxy

ligands, which does not seem unlikely in view of the well-known ability of Ce(IV) to complex alcohols and alkoxides.[11,12] The two reaction products would thus be formed by one-step, competing ligand-transfer reactions, with no benzyl cations involved as intermediates. The observed effect of added chloride ions could be explained as due to an increase of the ratio of chloro ligands to methoxy ligands, thus leading to a reduced ratio of methoxylation to chlorination.

Experimental Section

Most techniques and apparatus were as previously reported.[1] MeOH (Erba RS, water content 0.05%) and EtOH (Erba RSE, 99.9% pure) were used as received. The aromatic substrates (reagent grade chemicals) were purified by standard methods. CPC was prepared in good yield according to a literature method.[11]

General Oxidation Procedure. A solution of CPC (6.4 g, 12 mmol) in either MeOH or EtOH (150 mL) was flushed with nitrogen at room temperature (15 min), the proper methylbenzene (6 mmol) was added, and the resulting mixture was brought to boil by immersion in a preheated oil bath. After the red-orange color of Ce(IV) faded, the solution was rapidly cooled and poured into light petroleum that was thoroughly washed with water and dried (Na_2SO_4). The crude material obtained after removal of the solvent was eluted on acid-washed silica gel with $CHCl_3$/light petroleum 1:1. All isolated compounds were checked by GLC and found to be at least 99% pure.

Acknowledgments. The C.N.R. financial support is greatly acknowledged for the part of the work carried out at the University of Perugia. Thanks are also due to Professors E. Baciocchi and G. Illuminati for stimulating discussions.

Registry No.—**3**, 65915-93-7; CPC, 40888-83-3.

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Reaction of Singlet Oxygen with Enamino Lactones. Conversion of Lactones to α-Keto Lactones

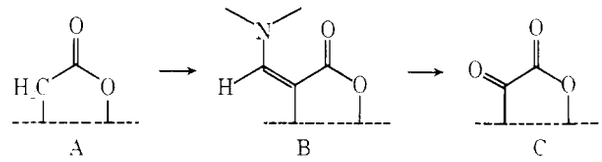
Harry H. Wasserman* and Jeffrey L. Ives

Department of Chemistry, Yale University, New Haven, Connecticut 06520

Received February 21, 1978

We have recently reported[1] a novel method for the conversion of ketones to α-diketones utilizing the facile cleavage of intermediate enamino ketones with singlet oxygen. The mildness and selectivity of this synthetic sequence prompted us to investigate its application to other carbonyl systems. We now report an extension of this procedure to the conversion of lactones to α-keto lactones.

Previous syntheses of α-keto lactones have generally been limited to the condensation of α-keto acids or esters with aldehydes followed by lactonization to α-keto-γ-butyrolactones.[2-5] These methods are often accompanied by side reactions such as dehydration of the intermediate γ-hydroxy-α-keto acids.[5] In our procedure, the α-keto lactones (both five- and six-membered cases) are formed *directly* from the parent lactones by a two-step process which, as outlined below, should have general applicability. The method involves conversion of the lactone A to the enamino lactone B by treatment with tris(dimethylamino)methane followed by oxidative cleavage of the enamine double bond with singlet oxygen to form the α-keto lactone C or its enol tautomer.



Our initial attempts to form the enamino intermediate B employed alkoxybis(dimethylamino)methane reagents along the lines of our earlier investigation on the oxidation of ketones to α-diketones.[1] Under these conditions, however, conversion to B was slow and often incomplete. We therefore used the more reactive DMF derivative, tris(dimethylamino)methane,[6] as recently reported by Martin and Moore[7] for the preparation of α-enamino butyrolactones.

Table I summarizes the systems studied, reaction conditions, and yields. All of the lactones (**1–6**) reacted readily with tris(dimethylamino)methane to yield the α-enamino derivatives (**7–12**). The second stage oxidative cleavage under conditions of dye-sensitized photooxygenation gave the desired α-keto lactones (**13–18**) in the yields shown. In all cases investigated, the α-keto lactones exist either exclusively or primarily in their enol forms.

Current interest in the preparation of α-methylene lactones[8] prompted us to explore the reaction of α-keto lactones **16** and **18** with phosphoranes under a large variety of reaction conditions[9] (temperature, solvent, reaction time, and method of ylide generation). Thus far, we have been unsuccessful in effecting a Wittig condensation with these systems. Under all conditions studied, the relatively acidic enol was rapidly and irreversibly deprotonated by the ylide to give, upon workup, only polymeric material, starting keto lactone, and traces of triphenylphosphine oxide.

We are currently studying further extensions of this synthetic sequence for the preparation of other α-keto carbonyl systems.

Experimental Section

Melting points were obtained in a Melt-Temp apparatus and are uncorrected. Infrared spectra were recorded in chloroform or neat using a Perkin-Elmer 700A spectrometer. NMR spectra were obtained with either a Perkin-Elmer R-32 90-MHz instrument or a Bruker 270-MHz instrument using tetramethylsilane as an internal standard. Mass spectra were recorded on a Hitachi RMU-6 spectrometer operated at 70 eV. Elemental analyses were performed by Dr. Robert Rittner, Olin Laboratories, New Haven, Conn.

Tris(dimethylamino)methane.[6] A mixture of 94.0 g (1.30 mol) of dimethylformamide and 57.0 g (0.53 mol) of dimethylcarbamyl chloride was heated at 120 °C under nitrogen for 24 h. The mixture was cooled to room temperature, and the resulting white crystals were filtered and washed several times with 100-mL portions of DMF and dried under vacuum for 48 h. A solution of 0.12 mol of lithium dimethylamide was prepared by adding 54 mL of a 2.2 M *n*-BuLi–hexane solution to a −78 °C solution of excess dimethylamine in 500 mL of THF followed by warming to 0 °C for 30 min. The solution was again cooled to −78 °C, and 13.5 g (0.10 mol) of the DMF–dimethylcarbamyl chloride adduct was added through Gooch tubing. The resulting slurry was stirred at room temperature for 18 h. Removal of solvent by distillation followed by vacuum distillation gave 7.4 g (51%) of the desired tris(dimethylamino)methane: bp 48 °C (12 mm) [lit.[6] bp 40–43 °C (12 mm)]; IR (neat) 3000–2700, 1475, 1450, 1345 cm^{-1}; NMR ($CDCl_3$) δ 3.05 (s, 1 H), 2.31 (s, 18 H); MS *m/e* 102, 44, 43.

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