showed it to consist of 46% of the *trans*-dibromo adduct, 44% of the *cis*-dibromo adduct, and 10% of the acetoxy bromide mixture. Distillation of the reaction mixture yielded 55% of *trans*-dibromide and 45% of *cis*-dibromide at 95–97 °C (200 torr). Anal. Calcd for $C_{10}H_{10}Br_2$: C, 41.41; H, 3.48; Br, 55.11. Found: C, 41.29; H, 3.50; Br, 54.96. The olefinic proton of the trans isomer is a singlet at δ 6.69 and that of the cis isomer occurs at δ 6.64. The peak at δ 6.51 was assigned to the olefinic proton of the acetoxy bromide product.

(2,4,6-Trimethylphenyl)acetylene. The reaction and workup were carried out as before. ^{1}H NMR analysis showed the reaction mixture to consist of 56% of the *trans*-dibromo adduct and 44% of the cis isomer. The olefinic protons of the two isomers are singlets at δ 6.68 and 6.5, respectively. No other products were found to be present.

Acknowledgment. The continued financial support of the Natural Science and Engineering Research Council of Canada is gratefully acknowledged as are the awards of scholarships to G.M.

Registry No. (4-Methoxy-2-methylphenyl)acetylene, 74331-69-4; (2,4-dimethylphenyl)acetylene, 16017-30-4; (2,5-dimethylphenyl)acetylene, 74331-70-7; (2-methylphenyl)acetylene, 766-47-2; (4-chloro-2-methylphenyl)acetylene, 74331-71-8; (5-chloro-2-methylphenyl)acetylene, 74331-72-9; (4-methoxy-2,6-dimethylphenyl)acetylene, 74331-73-0; (2,4,6-trimethylphenyl)acetylene, 769-26-6; (2,6-dimethylphenyl)acetylene, 74331-74-1; (4-bromo-2,6-dimethylphenyl)acetylene, 74331-75-2; 1-(2-methylphenyl)vinyl tosylate, 74331-76-3; 1-(2,6-dimethylphenyl)vinyl tosylate, 74331-77-4; 1-(2,6-dimethylphenyl)-1-bromoethene, 74331-78-5; 1-(2,6-dimethylphenyl)-1-chloroethene, 74331-79-6; 4-methylphenylacetylene, 766-97-2; (*E*)-1,2-dibromo-1-(2,4-dimethylphenyl)ethylene, 74331-80-9; (*Z*)-1,2-dibromo-1-(2,4-dimethylphenyl)ethylene, 74331-81-0; (*E*)-1,2-dibromo-1-(2,5-dimethylphenyl)ethylene, 74331-82-1; (*Z*)-1,2-dibromo-1-(2,5-dimethylphenyl)ethylene, 74331-83-2; (*E*)-1,2-dibromo-1-(2,4,6-trimethylphenyl)ethylene, 74331-84-3; (*Z*)-1,2-dibromo-1-(2,4,6-trimethylphenyl)ethylene, 74331-85-4; (*E*)-1,2-dibromo-1-(4-methylphenyl)ethylene, 74331-86-5; (*Z*)-1,2-dibromo-1-(4-methylphenyl)ethylene, 74346-16-0; (*E*)-1-acetoxy-2-bromo-1-(2,4-dimethylphenyl)ethylene, 74331-87-6; (*Z*)-1-acetoxy-2-bromo-1-(2,4-dimethylphenyl)ethylene, 74331-88-7; (*E*)-1-acetoxy-2-bromo-1-(2,5-dimethylphenyl)ethylene, 74331-89-8; (*Z*)-1-acetoxy-2-bromo-1-(2,5-dimethylphenyl)ethylene, 74331-88-7; 2,5-dimethyl-α-chlorostyrene, 74331-90-1; 2,4,6-trimethyl-α-chlorostyrene, 5312-67-4; 2,6-dimethyl-4-methoxy-α-chlorostyrene, 74331-91-2; 1-(2-methyl-4-methoxyphenyl)vinyl tosylate, 74331-92-3.

Notes

Oxidation by Metal Ions. 6.[1a] Intramolecular Selectivity in the Side-Chain Oxidation of *p*-Ethyltoluene and Isodurene by Cobalt(III), Cerium(IV), and Manganese(III)

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Received September 7, 1979

Side-chain substitutions of alkylaromatic compounds by one electron oxidants such as Ce(IV), Mn(III), and Co(III) are generally thought to occur via a radical cation intermediate[2,3] (eq 1a–c). However, this hypothesis has been

$$\mathrm{ArCH_3} + \mathrm{M}^{n+} \rightleftharpoons \mathrm{ArCH_3}^{+\cdot} + \mathrm{M}^{(n-1)+} \qquad (1a)$$

$$\mathrm{ArCH_3}^{+\cdot} + \mathrm{B} \rightarrow \mathrm{ArCH_2}\cdot + \mathrm{BH}^+ \qquad (1b)$$

$$\mathrm{ArCH_2}\cdot + \mathrm{M}^{n+} \xrightarrow[\text{steps}]{\text{one or more}} \text{products} + \mathrm{M}^{(n-1)+} \qquad (1c)$$

recently criticized.[4–6] It has been suggested that the benzyl radical may be directly formed by a hydrogen atom abstraction reaction (eq 2) promoted by one of the metal ligands.[4,6]

$$\mathrm{ArCH_3} + \mathrm{M}^{n+}\mathrm{L} \rightarrow \mathrm{ArCH_2}\cdot + \mathrm{M}^{(n-1)+} + \mathrm{HL} \qquad (2)$$

Certainly, the difficulty of reaching firm conclusions depends also upon the fact that many of the main features of these reactions are scarcely known. For example, in oxidation of poly(alkyl)benzenes, the effects of the oxidizing metal ions on the intramolecular selectivities (relative reactivity of nonequivalent α-hydrogen atoms) are virtually unknown.[7]

It is believed that such information could be very useful for a better understanding of the mechanism of these reactions and also be of practical interest. Therefore, a study has been carried out on the isomeric product distribution for the reactions in acetic acid of *p*-ethyltoluene and isodurene (1,2,3,5-tetramethylbenzene) with ceric ammonium nitrate (CAN), manganic acetate (in the presence of 0.2 M H_2SO_4[10]), and cobaltic acetate. For comparison, we have also investigated the side-chain bromination of the same substrates with *N*-bromosuccinimide (NBS) which certainly involves a hydrogen atom abstraction step.[12]

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(1) (a) Part 6 of the series Oxidation of Aromatic Compounds by Metal Ions. Part 5: Baciocchi, E.; Mei, S.; Rol, C.; Mandolini, L. *J. Org. Chem.* **1978**, *43*, 2919. Part 4: Maini, S.; Mandolini, L.; Rol, C. *J. Org. Chem.* **1978**, *43*, 3236. (b) Università di Perugia. (c) Università di Roma.

(2) Kochi, J. K. *Free Radicals* **1973**, *1*, 643–648, and references cited therein.

(3) (a) Benson, D. "Mechanisms of Oxidation by Metal Ions"; Elsevier: New York, 1976; p 2. (b) Heiba, E. I.; Dessau, R. M.; Koehl, W. J., Jr. *J. Am. Chem. Soc.* **1969**, *91*, 6830. (c) Baciocchi, E.; Mandolini, L.; Rol, C. *Tetrahedron Lett.* **1976**, 3343. (d) Hanotier, J.; Hanotier-Bridoux, M.; de Raditzky, P. *J. Chem. Soc., Perkin Trans. 2* **1973**, 381.

(4) Eberson, L.; Jönsson, J.; Wistrand, L. G. *Acta Chem. Scand., Ser. B* **1978**, *32*, 520.

(5) Hanotier, J.; Hanotier-Bridoux, M. J. *J. Chem. Soc., Perkin Trans. 2* **1973**, 1035.

(6) Eberson, L.; Oberrauch, E. *Acta Chem. Scand., Ser. B* **1979**, *33*, 343.

(7) Data of intramolecular selectivity are available only for the oxidation in acetic acid, under pressure at 105 °C, of *p*-cymene and *p*-ethyltoluene catalyzed by $Co(OAc)_2$[8] and for the reaction of Ce(IV) with isodurene.[9]

(8) Onopchenko, A.; Schulz, G. D.; Seekircher, R. *J. Org. Chem.* **1972**, *37*, 1414.

(9) (a) Baciocchi, E.; Mandolini, L.; Rol, C. *Tetrahedron Lett.* **1973**, 3787. (b) Baciocchi, E.; Rol, C.; Mandolini, L. *J. Org. Chem.* **1977**, *42*, 3682.

(10) In the absence of H_2SO_4 the reaction of alkylaromatics with Mn(III) occurs only at high temperature and can lead to products derived by attack of the carboxymethyl radical generated by the thermolysis of $Mn(OAc)_3$.[11]

(11) Heiba, E. I.; Dessau, R. M.; Koehl, W. G., Jr. *J. Am. Chem. Soc.* **1969**, *91*, 138.

Table I. Distribution of Isomeric Alcohols (Mole %) Obtained (See Text) from the Products of the Reactions of *p*-Ethyltoluene and Isodurene with Various Metal Ions and NBS

reagent and conditions	*p*-ethyltoluene 1	2	isodurene 3	4	5
$Co(OAc)_3$, AcOH, 60 °C	46.6 ± 0.4	53.4 ± 0.4	54.5 ± 0.9	23.0 ± 0.3	22.5 ± 0.6
CAN, AcOH, 60 °C	77.6 ± 1.2	22.4 ± 1.2	87.7 ± 0.6[a]	3.2 ± 0.2[a]	9.1 ± 0.7[a]
$Mn(OAc)_3$, 0.2 M H_2SO_4, AcOH, 20 °C	90.8 ± 1.0	9.2 ± 1.0	91.3 ± 1.0	2.2 ± 0.2	6.5 ± 0.8
NBS, AIBN,[b] CCl_4, 80 °C	93.8 ± 1.0	6.2 ± 1.0	58.6 ± 0.6	26.6 ± 0.3	14.8 ± 0.7

[a] We have previously reported 77% 3, 13% 4, and 10% 5 in the oxidation of isodurene with CAN.[9a] This discrepancy is probably due to some impurity of durene contained in the commercial sample of isodurene used in the previous work. The sample of isodurene used in the present work was obtained by synthesis (see Experimental Section). Eberson and Oberrauch[6] report for the oxidation of isodurene with CAN, under similar conditions, 79%, 7%, and 14% reaction at 2-, 1-, and 5-CH_3 groups, respectively. [b] 2,2′-Azobis(isobutyronitrile).

Table II. Reactivity Ratios of Nonequivalent α-Hydrogen Atoms in the Reactions of *p*-Ethyltoluene and Isodurene with Various Metal Ions and NBS

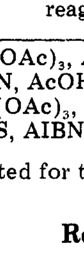
reagent and conditions	*p*-ethyltoluene $k_{C_2H_5}/k_{CH_3}$[a]	isodurene k_{2CH_3}/k_{1CH_3}[a]	k_{5CH_3}/k_{1CH_3}[a]	k_{2CH_3}/k_{5CH_3}
$Co(OAc)_3$, AcOH, 60 °C	1.31 ± 0.02	4.7 ± 0.2	1.9 ± 0.1	2.4 ± 0.1
CAN, AcOH, 60 °C	5.2 ± 0.4	55 ± 4	5.7 ± 0.8	9.6 ± 0.7
$Mn(OAc)_3$, 0.2 M H_2SO_4, AcOH, 20 °C	15 ± 2	83 ± 9	5.9 ± 1.4	14 ± 2
NBS, AIBN, CCl_4, 80 °C	23 ± 4	4.4 ± 0.1	1.11 ± 0.07	4.0 ± 0.3

[a] Corrected for the statistical factor.

Results and Discussion

The oxidation reactions have been carried out in acetic acid under nitrogen at 60 °C with CAN and $Co(OAc)_3$ and at 20 °C with the much more reactive $Mn(OAc)_3$/0.2 M H_2SO_4. In the reactions of *p*-ethyltoluene and isodurene with $Co(OAc)_3$ and $Mn(OAc)_3$/0.2 M H_2SO_4, the products are benzyl acetates accompanied by small amounts (1–5%) of carbonyl compounds (mainly aldehydes, according to the ^1H NMR spectrum). With CAN, benzyl acetates and nitrates are formed, again accompanied by small amounts of carbonyl compounds.[9]

The isomeric product distributions in the above reactions and thereby the intramolecular selectivity were determined by reducing the crude reaction product with $LiAlH_4$ in order to convert *all* the side-chain substituted compounds (acetates, carbonyl compounds, and, in the case of Ce(IV), nitrates) into the corresponding benzyl alcohols, **1** and **2** from *p*-ethyltoluene and **3**–**5** from isodurene, which were then analyzed by VPC. The benzyl bromides obtained in the reactions of *p*-ethyltoluene and isodurene with NBS were also converted into the benzyl alcohols. The distributions of the alcohols **1**–**5** are reported in Table I.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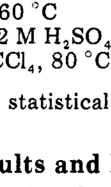
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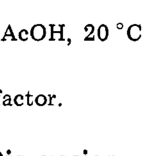
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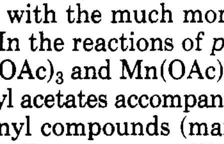
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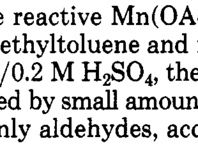
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From the data of Table I a more detailed picture of the intramolecular selectivities can be obtained by calculating the reactivity ratios (statistically corrected) for nonequivalent benzylic C–H bonds. Thus, from the distribution of alcohols **1** and **2**, the reactivity ratio $k_{C_2H_5}/k_{CH_3}$, which represents the secondary/primary α-hydrogen selectivity, can be determined. Analogously, from the distribution of the isomeric alcohols **3**–**5** in the reactions of isodurene, the reactivity ratios k_{2CH_3}/k_{1CH_3}, k_{2CH_3}/k_{5CH_3}, and k_{5CH_3}/k_{1CH_3} can be calculated. (The numbers indicate the position of the methyl group in the isodurene molecule.) All these ratios are collected in Table II.

The intramolecular selectivities of the three metals are substantially different. However, it must be noted that *all* the reactivity ratios of Table II increase regularly among the metals in the order Co(III) < Ce(IV) < Mn(III).[13] This suggests that the three metal salts, under the given conditions,[14] probably react by the same mechanism and that this mechanism is operating with both *p*-ethyltoluene and isodurene. If the mechanisms were different, it would be a quite fortuitous coincidence that the factors determining the selectivity values for each metal keep their relative weight unchanged as the substrate nature and the type of selectivity under consideration (secondary/primary vs. positional) are varied.

The results of the reactions with NBS do not conform with the correlation that exists among the metals;[15] thus,

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(12) Pearson, R. E.; Martin, J. C. *J. Am. Chem. Soc.* **1963**, *85*, 3142.

(13) The fact that the temperature is not the same for all the reactions investigated should be considered. However, according to previous experiments,[9b] intramolecular selectivity is not expected to be very significantly affected by changes in temperature.

(14) Of course, we are perfectly aware that the ligands and the acidity of the solution can have a significant effect on the oxidation potentials, the reactivity, and the selectivity of the metal ions. Therefore, the validity of our conclusion is limited to the particular metal salts used under the given experimental conditions.

(15) Interestingly, when we plot log (k_{5CH_3}/k_{1CH_3}) and log (k_{2CH_3}/k_{5CH_3}) vs. log (k_{2CH_3}/k_{1CH_3}), the data for the three metals define two straight lines, passing through the origin, which are not fit by the corresponding data for NBS. While this would certainly support the conclusion that Co(III), Ce(IV), and Mn(III) react by a mechanism different from that of NBS, we do not wish, at present, to put too much emphasis on such free-energy linear relationships since we are aware of the fact that even small experimental errors could significantly influence the very high reactivity ratios for the reactions of Mn(III) and Ce(IV).

NBS exhibits the *highest* value of the $k_{C_2H_5}/k_{CH_3}$ ratio but the *lowest* values of the k_{2CH_3}/k_{1CH_3} and k_{5CH_3}/k_{1CH_3} ratios. A further different situation is observed for the k_{2CH_3}/k_{5CH_3} ratio: in this case NBS is more selective than Co(III) but less selective than Ce(IV) and Mn(III). These findings are not easily explainable unless one assumes that the factors determining the selectivity and its dependence upon the substrate structure for the reactions with NBS are substantially different from those operating in the reactions of Co(III), Mn(III), and Ce(IV). A reasonable conclusion is therefore that the three metals react by a mechanism different from the free-radical one occurring in the reactions with NBS. Most probably, this mechanism is the radical cation mechanism reported in eq 1a–c, which is also supported by the significant substrate selectivity generally exhibited by the reactions of these metals.[3b,c]

In the radical cation mechanism, the intramolecular selectivity has its origin in step 1b and the two main factors determining the transition-state structure of this step should be the positive-charge distribution (the base preferentially attacking the alkyl group bonded at the ring position with the highest positive-charge density)[3b,6,9b] and the stability of the formed free radical. The weight of the former factor is more important for reactant-like transition states, that of the latter for product-like transition states. The different values of selectivity exhibited by Co(III), Mn(III), and Ce(IV) can therefore be ascribed to differences in the nature of the base involved in step 1b, which result in different positions of the transition state along the reaction coordinate. Consequently, the relative weight of the two above mentioned factors may change in going from one metal to another. Probably, the species acting as the base in step 1b is not the solvent but a counter ion paired to the radical cation; the nature of this counter ion, of course, closely depends on that of the oxidizing system.

In the reaction of isodurene, the stability of the benzyl free radicals follows the order $2 > 1 \simeq 5$, while for the positive charge distribution in the ring, recent calculations give the order $5 \geq 2 > 1$.[6,16] This explains why, in all cases, the methyl group at position 2 is the most reactive one and the k_{5CH_3}/k_{1CH_3} ratio is always significantly larger than unity, while a virtually statistical distribution could be predicted for this ratio on the basis of the stability of the corresponding free radicals, as it is found in the reaction with NBS. In the *p*-ethyltoluene radical cation, the two factors oppose each other since the positive-charge density should be higher in the ring position adjacent to the methyl group (hyperconjugative effect[17]), whereas the secondary benzyl radical is much more stable than the primary one. It appears therefore that the free-radical stability factor always outweighs the charge-density factor, even though to an extent decreasing in the order Mn(III) > Ce(IV) > Co(III).[18]

Experimental Section

^{1}H NMR spectra were taken on a JEOL JNM-C60HL spectrometer, using Me_4Si as the internal standard. IR spectra were obtained on a Perkin-Elmer 257 from 2% solutions in $CHCl_3$. VPC analyses were performed on a GI Fractovap (C. Erba) chromatograph connected to a Hewlett-Packard 18850a GC terminal. All melting points are uncorrected.

Materials. Ceric ammonium nitrate [$(NH_4)_2Ce(NO_3)_6$] (Merck, 99% pure) was dried at 85 °C for 1 h. Solutions of cobaltic acetate in acetic acid were prepared by oxidation of cobaltous acetate with ozone.[19] The conversion of Co(II) into Co(III) was determined by iodometric titration to be 99 ± 1%. Manganic acetate [$Mn(OAc)_3 \cdot 2H_2O$] was prepared according to a literature method.[11] The product was found to be 98 ± 2% pure (iodometric titration). *N*-Bromosuccinimide (Erba, 99% pure) was recrystallized from hot water. 2,2′-Azobis(isobutyronitrile) (Merck, 98% pure) was recrystallized from 50% aqueous ethanol. *p*-Ethyltoluene (Fluka, 98% pure), mesitylene (Erba, 99% pure), *p*-methylacetophenone (Fluka, 98% pure), and *p*-bromoethylbenzene (Fluka, 98% pure) were commercial samples and used as received. Acetic acid (Erba RP, 99.8% pure) was thoroughly purged with pure nitrogen before use. 2,4,6-Trimethylbenzyl alcohol (**3**), 2,3,5-trimethylbenzyl alcohol (**4**), and 3,4,5-trimethylbenzyl alcohol (**5**) were available from a previous investigation.[9b] Isodurene was synthesized according to a literature method.[20]

Methyl-*p*-tolylcarbinol (1) was obtained by reduction of *p*-methylacetophenone with $LiAlH_4$ in dry ether. The product was a colorless liquid, more than 99.5% pure by VPC: bp 101–102 °C (15 mmHg) [lit.[21] bp 120 °C (19 mmHg)]; $n^{17}{}_D$ 1.5248 (lit.[22] $n^{20}{}_D$ 1.5246).

***p*-Ethylbenzyl Alcohol (2).** Carbonation of the Grignard reagent derived from *p*-bromoethylbenzene gave *p*-ethylbenzoic acid [mp 113–115 °C (lit.[23] mp 113.5 °C)] which, after reduction with $LiAlH_4$, gave the title compound as a colorless liquid more than 99.5% pure by VPC: IR 3590 and 3420 cm^{-1}; ^{1}H NMR (pure liquid) δ 7.19 (d, 2 H, J = 7.5 Hz), 7.01 (d, 2 H, J = 7.5 Hz), 5.02 (s, 1 H), 4.44 (s, 2 H), 2.50 (q, 2 H, J = 6.5 Hz), 1.16 (t, 3 H, J = 6.5 Hz).

Oxidation with CAN. A mixture of the hydrocarbon (2.5 mmol) and CAN (5.0 mmol) in 60 mL of acetic acid was stirred at 60 °C in a nitrogen atmosphere in the dark until the red-orange color faded (40 min with isodurene and 15 h with *p*-ethyltoluene). The reaction mixture was then cooled and poured into light petroleum. The solution was washed with water and dried with anhydrous Na_2SO_4.

Oxidation with Cobaltic Acetate. The aromatic substrate (2.5 mmol) was added to 25 mL of a 0.2 M solution of cobaltic acetate. The oxidation reaction was carried out at 60 °C. After being cooled to room temperature, the reaction mixture was worked up as above. The reaction time was 25 min (30% conversion based on iodometric titration) with *p*-ethyltoluene and 10 min with isodurene (50% conversion).

Oxidation with Manganic Acetate. A typical procedure was as follows. Manganic acetate (5.0 mmol) was dissolved in 100 mL of acetic acid. The solution was then treated with H_2SO_4 (1.3 mL). The aromatic substrate (2.5 mmol) in acetic acid (25 mL) was rapidly added with stirring to the oxidant solution. After about 20 s, the reaction was quenched with cold water/chloroform and worked up as above. With *p*-ethyltoluene the conversion was 40% (iodometric titration), while with isodurene it was 75%. With longer reaction times the formation of significant amounts of diarylmethanes was observed, probably due to acid-catalyzed reaction of the formed benzyl acetates with unreacted hydrocarbon.

Bromination with NBS. Typically, the aromatic hydrocarbon (10 mmol) was reacted with NBS (3 mmol) in refluxing CCl_4 under nitrogen in the presence of azobis(isobutyronitrile) (AIBN, 40 mg). The reaction time was 18 h for *p*-ethyltoluene and 3 h for isodurene. Workup was as previously reported.[12]

Determination of Isomeric Distributions. The crude materials derived from the oxidation with metal ions were reduced with excess $LiAlH_4$ in dry ether. Similarly, the benzyl bromides coming from the reactions with NBS were hydrolyzed with Ag_2O in water/1,4-dioxane at 100 °C over 6 h. The resulting mixtures

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[16] An order 2 > 5 > 1 is also reported. Nyberg, K. *Acta Chem. Scand.* **1971**, *25*, 2499.

[17] For a recent discussion on hyperconjugation see: Glyde, E.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1977**, 678.

[18] However, this is not always the case, since in the Co(III)-catalyzed oxidation of some dialkylbenzenes with oxygen,[8] the relative ease of oxidation of the alkyl groups follows the sequence methyl > ethyl > isopropyl. Similarly, exclusive formation of *p*-isopropyl acetate has been observed (Giordano, C.; Belli, A.; Citterio, A.; Minisci, F. *J. Org. Chem.* **1979**, *44*, 2314) in the oxidation of *p*-cymene by peroxy disulfate in the presence of Cu(II) salts.

[19] Kamiya, Y.; Kashima, H. *J. Catal.* **1972**, *25*, 326.

[20] Horning, E. C. "Organic Syntheses"; Wiley: New York, 1943; Collect. Vol 2, p 360.

[21] Sulzbacker, M.; Bergmann, E. *J. Org. Chem.* **1948**, *13*, 303.

[22] United Gas Improv. Co. U.S. Patent 2293774, 1939.

[23] Nystrom, R. F.; Brown, G. *J. Am. Chem. Soc.* **1947**, *69*, 2548.

of benzyl alcohols were analyzed by VPC, using a 3-mm i.d. glass column (1.8 m) containing 0.1% FFAP on carbon-coated beads with nitrogen as the carrier gas at 110 °C.

Acknowledgment. We are grateful to the Consiglio Nazionale delle Ricerche, C.N.R., for financial support. We also thank Professor Lennart Eberson for making available material to us prior to publication.

Registry No. 1, 536-50-5; 2, 768-59-2; 3, 4170-90-5; 4, 50849-01-9; 5, 39126-11-9; *p*-methylacetophenone, 122-00-9; *p*-bromoethylbenzene, 1585-07-5; *p*-ethylbenzoic acid, 586-76-5; $Co(OAc)_3$, 917-69-1; $Mn(OAc)_3$, 993-02-2; $(NH_4)_2Ce(NO_3)_6$, 16774-21-3.

Reactivity and Synthesis of the 1,6-Dioxa-6aλ⁴-thia-3,4-diazapentalene System[1]

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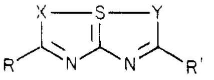
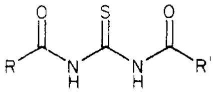
Received March 13, 1980

Recent reports[2,3] of the preparation of 2,5-diaryl-1,6-dioxa-6aλ^4-thia-3,4-diazapentalenes by aroylation of 5-amino-1,2,3,4-thiatriazole have made this interesting heteropentalene system readily available for study. In addition, the authors point out that compounds such as **1** may be converted into di- and trithia derivatives **2** and **3** by treatment with phosphorus pentasulfide.



	R	R'	X	Y
1	Ph	Ph	O	O
2	Ph	Ph	S	O
3	Ph	Ph	S	S
4	CH_3	CH_3	O	O
5	Ph	CH_3	O	O

We recently had occasion to react **1** with P_2S_5 in dioxane, hoping to obtain **2** as the major product. For this reason, the reaction was done at ca. 90 °C rather than at reflux. A mixture of **2** and **3** plus an unexpected third product which proved to be 1,3-dibenzoylthiourea (**6**) was produced. Indeed when the reaction was done at 70 °C, **6** was the sole product, isolated in 91% yield.



	R	R'
6	Ph	Ph
7	CH_3	CH_3
8	Ph	CH_3

The mechanism of this reduction is not clear but apparently is not due to small amounts of hydrogen sulfide associated with the P_2S_5 since bubbling H_2S through a dioxane solution of **1**, with and without added sulfur, at temperatures from 50 °C to reflux gave no reaction. Further, attempts to effect the reduction with sodium borohydride gave complex mixtures with only traces of **6**. There are reports of phosphorus pentasulfide acting as a reducing agent to convert sulfoxides[4] and sulfilimines[5] to the corresponding sulfides. These authors propose a four-centered mechanism to transfer the sulfoxide oxygen to phosphorus with formation of $P_4O_4S_6$, the sulfide, and elemental sulfur, possibly via the thiosulfoxide. A completely analogous mechanism is obviously not operating in the present example since the transfer of a heteratom is not involved. However, it is likely that elemental sulfur is produced during the reaction along with a phosphorus sulfide containing a reduced percentage of sulfur. No attempt has been made to isolate or identify these byproducts.

Since the formation and reduction of **1** can be done very easily and in high yield, this sequence represents a useful synthesis of symmetrical 1,3-diaroylthioureas. It is interesting to note that 1,3-dibenzoyl-2-thiourea has not been previously reported.

The reduction of **1** to **6** suggested the reverse process, namely, an oxidation, as a synthetic method to **1**. This proved to be possible by using bromine as an oxidizing agent to instantly convert **6** into **1** in 73% yield. For the synthesis of symmetrical diaryl compounds such as **1**, the reaction of aroyl chlorides with 5-amino-1,2,3,4-thiatriazoles is most convenient since the acid chlorides are more readily available than the thioureas. However, in the case of unsymmetrically substituted compounds, or those with alkyl substituents, the thiatriazole method is reported to fail.[2] 1,3-Diacetyl-[6] (**7**) and 1-acetyl-3-benzoyl-2-thioureas[7] (**8**) were smoothly converted into **4** and **5**, respectively, by bromine oxidation to test the oxidative cyclization method in these instances. The oxidative cyclizations were carried out at room temperature by adding 1 equiv of bromine dropwise to a chloroform solution of the thiourea containing 2 equiv of triethylamine.

Experimental Section

Melting points were determined in open capillaries and are uncorrected. NMR spectra were measured at 60 MHz in $CDCl_3$. Mass spectra were determined with a Varian-MAT CH_4 spectrometer. Percolations were done with Merck silica gel 60. Microanalyses were performed by the analytical department of Syntex Research. Anhydrous magnesium sulfate was used to dry all organic solutions.

Reaction of 1 with P_2S_5 at 90 °C. A mixture of 5 g (18 mmol) of **1**[2,3] and 10 g (45 mmol) of P_2S_5 in 200 mL of dioxane was stirred under N_2 at 90 °C for 1 h. The reaction mixture was cooled and filtered, and the filtrate evaporated. The residue was passed through a pad of silica gel. Elution with 20% hexane/CH_2Cl_2 afforded an orange substance which crystallized from toluene to give 0.8 g (16%) of **3**: mp 207.5-209.0 °C (lit.[3] mp 208-209 °C); mass spectrum, *m/e* 314 (M^+).

Elution with CH_2Cl_2 gave an essentially colorless material which crystallized from EtOH to yield 0.6 g (12%) of **2**: mp 152-154 °C (lit.[3] mp 152-153 °C); mass spectrum, *m/e* 298 (M^+).

Elution with 1% MeOH/CH_2Cl_2 gave material which crystallized from EtOH to give 1 g (20%) of **6** as yellow needles: mp 166-169 °C; NMR δ 7.4-7.7 (3 H, m), 7.9-8.1 (2 H, m); mass spectrum, *m/e* 284 (M^+). Anal. Calcd for $C_{15}H_{12}N_2O_2S$: C, 63.36; H, 4.25; N, 9.85; S, 11.28. Found: C, 62.98; H, 4.32; N, 9.73; S, 11.15.

Reaction of 1 with P_2S_5 at 70 °C. A mixture of 0.5 g (1.8 mmol) of **1**[2,3] in 20 mL of dioxane with 1 g (4.5 mmol) of P_2S_5 was stirred under N_2 in an oil bath at 70 °C for 1.5 h. The reaction mixture was cooled and filtered and the filtrate evaporated. The residue was passed through a pad of silica gel with CH_2Cl_2 and

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[1] Contribution No. 559 from the Institute of Organic Chemistry, Syntex Research, Palo Alto, CA.

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