Table VII, which lists compounds containing a coplanar zigzag chain, shows that the S value of the OH-3α radical is not constant but depends on the kind of Y-2β group. On the other hand, Table VIII, which lists compounds containing a noncoplanar chain, shows that the S value of the OH-3β radical is constant and independent of the kind of Y-2α group. One concludes that, although the direct distance between the Y-2 group and the OH-3 radical is much larger in the coplanar zigzag chain, *i.e.*, in the trans conformation, than in the noncoplanar structure, *i.e.*, in the gauche conformation, the influence of the Y-2 group is easily transmitted to the OH-3 radical only through a coplanar zigzag chain.

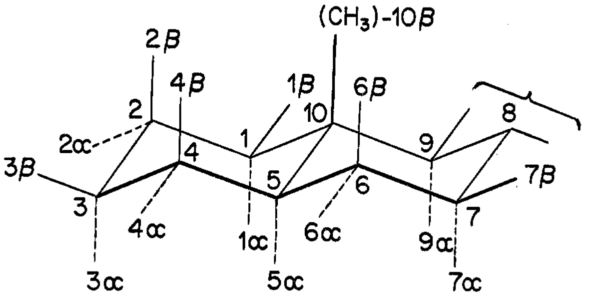

Figure 14.—Steroid skeleton.

Conclusion

Several theories (or calculation methods) have been presented for estimating the optical rotation of an organic compound.[32] Some of these emphasize the role of the atomic refraction, R_{D} (or polarizability, α), of an atom (or a radical) in producing the optical rotatory power of a molecule. However, none of them pay any attention to the variability of or the nature of the change in this R_{D} (or α) value. Moreover, since the days of van't Hoff,[33] the role apparently played by the presence or absence of a coplanar zigzag chain has never been noticed. It is hoped that the empirical rules 1–8 presented in this article will be of help in constructing a new theory or developing new approaches to the calculation of optical rotatory power.

Addendum.—The fact that a straight $[M]^{20}{}_{\mathrm{D}}$ *vs.* S line changes its slope, according to the change in the kind of a Y atom (or radical) which is coplanar with the X atom (or radical) in the same molecule, means that these two atoms (or radicals) (*i.e.*, X and Y) couple with each other to produce a certain partial molecular rotation, in spite of their existence in one plane (*cf.* **7″**, **9′**, and **10′**; **11**, **14**, **16**, and **17**; **11′**, **16″**, and **17″**, etc.).

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Nonclassical Oxidation of Aromatics. I. Cobaltic Ion Catalyzed Oxidations of *p*-Cymene, *p*-Ethyltoluene, and *sec*-Butyltoluenes[1]

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Co(III) ion catalyzed oxidation of alkyltoluenes with oxygen was studied under mild conditions. It was found that the methyl group was preferentially oxidized in the presence of other groups on the same benzene ring. *p*-Cymene afforded *p*-isopropylbenzoic acid (90%) and *p*-methylacetophenone (10%) as the primary products. *p*-Ethyltoluene gave *p*-ethylbenzoic acid (68%) and *p*-methylacetophenone (25%) as major products. Prolonged oxidation converted *p*-methylacetophenone into *p*-acetobenzoic acid and eventually into terephthalic acid. A mixture of the isomeric *sec*-butyltoluenes was oxidized to the corresponding *sec*-butylbenzoic acids (89%). The relative ease of oxidation of the alkyl groups follows the sequence methyl > ethyl > isopropyl ∼ *sec*-butyl. These results cannot be rationalized on the basis of the classical free-radical mechanism, and an electron-transfer mechanism involving the intermediacy of radical cations is proposed.

The literature has numerous references to the oxidation of various alkyltoluenes in which secondary or tertiary hydrogen on alkyl groups is preferentially abstracted. In fact, the oxidation of the methyl group in such instances is difficult. Products are comprised of carboxylic acids, hydroperoxides, and/or cleavage products of the latter. Oxidation of *p*-cymene or *p*-ethyltoluene with 15% nitric acid is reported to produce *p*-toluic acid, whereas *p*-ethylisopropylbenzene affords *p*-ethylbenzoic acid.[2] In the autoxidation of *p*-ethyltoluene[3] or *p*-cymene,[4–7] major products were either *p*-toluic acid, terephthalic acid, *p*-methylacetophenone, or a combination of these. *p*-Acetobenzoic acid, *p*-isopropylbenzoic acid, and *p*-(α-hydroxyisopropyl)benzoic acid were also formed in varying amounts. The relative ease of oxidation of these alkyl groups follows the sequence isopropyl > ethyl > methyl. In this paper, we report on a study of Co(III) ion catalyzed oxidation of a methyl group in preference to isopropyl, ethyl, or *sec*-butyl in *p*-cymene, *p*-ethyltoluene, and *sec*-butyltoluenes. Results obtained are surprising as the normal order of hydrogen abstraction, tertiary > secondary > primary, is reversed.

Results

Reactants, experimental conditions, and the results obtained are summarized in Table I. Conversion in all experiments was essentially 100%.

Oxidation of *p*-cymene gave *p*-isopropylbenzoic

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(4) V. B. Fal'kovskii and L. A. Golubko, *Neftekhimiya*, **8** (3), 392 (1968).

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TABLE I

OXIDATION OF ALKYLTOLUENES[a]

Expt no.	1	2[b]	3	4
Hydrocarbon oxidized	p-Cymene		p-Ethyltoluene	sec-Butyltoluenes[c]
Reactants, g				
$Co(OAc)_2 \cdot 4H_2O$	20	20	20	20
MEK	20	20	20	20
HOAc	400	400	400	400
n-C_4H_{10}	70	85	60	100
Substrate	53	60	20	62
Conditions				
Induction time, hr	1.0	0.5 min	0.7	0.5
Reaction time, hr	1.5	1.5	0.7	1.5
Products, g (%)				
p-Isopropylbenzoic acid	58.5 (90)	10.6 (19)		
p-Acetobenzoic acid	6.5 (10)	4.0 (7.3)	0.7 (2)	
p-Ethylbenzoic acid			16 (68)	
sec-Butylbenzoic acids				66.0 (89)[d]
p-Toluic acid		9.3 (17)	1.3 (5.5)	
p-Methylacetophenone		30 (55)	5.5 (25)	
Terephthalic acid		1.0 (1.8)	Trace	

[a] 105°, 22 atm total pressure (partial pressures of butane and oxygen). [b] 20 g of LiCl added. [c] 36.5% para, 59.0% meta, and 4.5% ortho. [d] 38.3% para, 59.5% meta, and 2.2% ortho.

acid and *p*-acetobenzoic acid in yields of 90 and 10%, respectively. To determine whether *p*-acetobenzoic acid was formed in competition with *p*-isopropylbenzoic acid, or as the result of secondary oxidation of the latter, one experiment was interrupted after 30 min. *p*-Isopropylbenzoic acid was shown in this case to be the only acid formed along with *p*-methylacetophenone. Formation of ketone is evidence for the competitive nature of the reaction. Prolonged oxidation of *p*-cymene for 5.5 hr resulted in significant amounts of terephthalic acid.

Oxidation of *p*-ethyltoluene under similar conditions gave *p*-ethylbenzoic acid and *p*-methylacetophenone in yields of 68 and 25%, respectively.

A mixture of *sec*-butyltoluenes (36.5% para, 59.0% meta, and 4.5% ortho) gave an 89% yield of the corresponding *sec*-butylbenzoic acids.

These results demonstrate unique and unexpected selectivity in methyl group attack in preference over other types of alkyl groups on the same benzene ring.

Discussion

The system discussed involves two basic reactions: (a) continuous conversion of Co(II) ions to Co(III), and (b) interaction of Co(III) with the aromatic substrates in the presence of oxygen. The first proceeds in the presence of methyl ethyl ketone (MEK)[9], or other promoters. As the ketone is rapidly consumed, *n*-butane was generally used as its precursor and a promoter of greater permanency to ensure complete conversions. Co(II) ions formed in the course of the second reaction are regenerated to Co(III) in the first. If neither ketone nor butane is added, Co(III) ions can be formed by interaction of Co(II) with peroxy radicals derived from the substrate alone.[8-12]

$$PhCH_2OO\cdot + Co(II) \longrightarrow PhCHO + Co(III) + OH^-$$

The major products of alkyltoluene oxidation in our work are unexpected on the basis of the classical free radical theory. A different mechanism, possibly involving an electron transfer step, may be operating. Such a mechanism, proposed by Dewar on kinetic grounds for the oxidation of *p*-methoxytoluene with Mn(III)[13] ions, apparently also applies to Co(III).[14] It would explain the fact that in *p*-xylene oxidation, in the presence of large amounts of cobaltic acetate and acetic acid solvent, the reaction does not stop at the *p*-toluic acid stage as in the oxidation using catalytic amount of cobalt salt. Attempts to rationalize this observation in terms of accepted free radical theory are inconclusive.[13,15] Recently, certain radical cations derived from methyl and *tert*-butyl substituted benzenes employing Co(III) salts have been observed directly by esr,[16] indicating electron transfer in the absence of oxygen. Additionally, oxidation of alkylbenzenes with potassium 12-tungstocobaltate(III) ions ($K_5CoO_4W_{12}O_{36}$) imply involvement of outer-sphere electrons in radical cation formation.[17] Heiba, *et al.*,[14] and others[18,19] used the magnitude of ρ values in the Hammett σ–ρ relationship to distingush attack by Co(III) ions from the normal radical abstraction. Among their criteria for an electron-transfer mechanism are the following: (a) requirement of high concentration of metal ions in a higher valency state, (b) failure of the reactivities of aromatics to follow the normal order of hydrogen abstraction, (c) small effect of cupric ions, effective inhibitors through electron transfer, and (d) acceleration of rate by chloride ions, accompanied in some cases by nuclear and side chain chlorinations. Because of the similarity of the ρ values obtained in both the absence and presence of oxygen (-2.4^{14} *vs.*

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−2.66[18]), electron transfer from toluene to Co(III) was probably involved.

Some of the above criteria were applied to our studies with oxygen. Table II demonstrates the effect of catalyst concentration on cymene conversion and induction period. With increasing cobalt concentration, a shortening of the induction time, as well as increasing cymene conversion, was obtained, with no effect on the selectivity to isopropylbenzoic acid. The distinguishing feature of this system is its requirement for a high concentration of metal ions throughout the reaction, not observed in free-radical processes where the metal catalyst is only effective in the early stages of the reaction.[20,21] Similar conditions are also employed in novel xylene oxidations,[22] believed to involve radical cation intermediates (Teijin process).[23] Table III summarizes reactivities for some aromatics which were obtained by competitive oxidation. Reactivity data of Table III should be compared with literature values of Table IV. Reactivities observed in Co(III) systems differ from those observed with Cr(VI) where a hydrogen abstraction pattern was followed. In the Mn(III) system, the electron transfer pathway appears to be of importance only in highly activated molecules such as *p*-methoxytoluene. The reactivity sequence observed by us for alkylbenzenes, ethylbenzene > toluene > cumene, is in accord with the literature. Similarly, the reactivity order of *p*-cymene > *p*-*tert*-butyltoluene and their magnitude are also in reasonable agreement with the literature.[18] *p*-Xylene under our conditions was less reactive than previously reported.[14]

TABLE II

EFFECT OF CATALYST CONCENTRATION ON *p*-CYMENE CONVERSION[a,b]

Catalyst[c] concn, *M*	Cymene conversion, %	Induction period, hr
0.18	100	1.0
0.09	18	3.5
0.04	2	11.0

[a] 1.2 *M* cymene and 1.0 *M* C_4H_{10} were used in cooxidation (105°, 22 atm, 1.5 hr). [b] Initiated with MEK. [c] Total cobalt ions, initially added as $Co(OAc)_2 \cdot 4H_2O$.

TABLE III

RELATIVE REACTIVITIES OF AROMATICS TOWARD Co(III) ION[a]

p-Xylene	3.9[b]
p-Ethyltoluene	3.5
p-Cymene	2.4
o-Xylene	2.0
p-*tert*-Butyltoluene	1.9
Ethylbenzene	1.2
Toluene	1.0[c]
Cumene	0.1
p-Methylacetophenone	0.1
tert-Butylbenzene	0.0[d]

[a] 105°, 22 atm, in presence of MEK–C_4H_{10}. [b] Reactivity per molecule. [c] Assumed standard. [d] Internal standard.

Even more interesting than this reactivity sequence is the competition between the methyl group and other alkyl substituents in the alkyltoluenes. Assuming that reactivity of the isopropyl group in cymene is represented by half the molar amount of *p*-acetobenzoic acid formed, and reactivity of the methyl group by the sum of the molar amount of *p*-isopropylbenzoic acid and half that of *p*-acetobenzoic acid produced, the methyl group reacts about 19 times faster than isopropyl. Applying this reasoning to *p*-ethyltoluene, its methyl group reacts about twice as fast as ethyl, even though ethylbenzene is slightly more reactive than toluene.

TABLE IV

REACTIVITIES OF AROMATICS TOWARD Co(III), Cr(VI), AND Mn(III) IONS AND SOME RADICALS (PER ACTIVE HYDROGEN)

Aromatic Hydrocarbon	Co(III), 65°[a]	Cr(VI), 30°[d]	Mn(III), 130°[f]	ROO·, 90°[g]	Cl·, 40°[h]
Toluene	1.0[b]	1.0	1.0	1.0	1.0
Ethylbenzene	1.3[b]	3.1		7.8	2.5
Cumene	0.3[b]			13.3	5.5
Diphenylmethane	0.8[c]	6.3	7.9	16.0	2.0
Triphenylmethane	0.7[c]	8.1	13.2		7.2
p-Methoxytoluene	71[b]		92[b,e]		

[a] Reference 14. [b] Per molecule. [c] Per active hydrogen, 40°.[19] [d] K. B. Wiberg, *Tetrahedron*, **8**, 313 (1960). [e] Our own extrapolation. [f] E. I. Heiba, R. M. Dessau, and W. J. Koehl, Jr., *J. Amer. Chem. Soc.*, **91**, 138 (1969). [g] G. A. Russell, *ibid.*, **78**, 1047 (1956). [h] G. A. Russell, *ibid.*, **85**, 2976 (1963).

A recent paper[24] describes anodic oxidation of *p*-cymene in methanol *via* electron transfer to products corresponding to a reactivity of the isopropyl group as compared to methyl of about 2:1. The Co(III) system is therefore milder and more selective than electrochemical oxidation. Its selectivity can be altered by addition of chloride ions.[14] The accelerating effect of chloride ion and ensuing loss in selectivity associated with a more vigorous oxidation is exemplified by experiment 2. Under such conditions, reactivity of isopropyl group *vs.* methyl was 3.2:1, similar to values obtained in free radical oxidations [3.5:1[25] and 3.2:1 (ref *g*, Table IV)]. No ring or side chain chlorinated products were found. Chloride ion concentration was possibly not sufficient to capture the reactive radical cation, or the mechanism may have changed.

Based on the literature and our own work, a mechanism is proposed which involves the following steps: (a) interaction of Co(III) with the alkyltoluenes to form radical cations, (b) loss of α hydrogen to form radicals, (c) trapping of radicals by oxygen to form peroxy radicals, and (d) termination of peroxy radicals.

The first step involves reversible interaction of Co(III) ions with the substrate to form radical cations. This is based on the observation that the rate of oxidation can be accelerated or slowed down by adding Co(III) or Co(II) ions, respectively. In the next step, benzyl radicals are formed from the radical cation intermediate by loss of α hydrogen as protons. The loss of proton is controlled by stereoelectronic considerations and not by the thermodynamic stability of the product. The rate-determining step could be either K_{eq} or k_2, or both, depending on the ionization potential of the substrate and the stability of radical cation formed.

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(20) Z. G. Kozlova, V. F. Tsepalov, and V. Ya. Shlyapintokh, *Kinet. Catal. (USSR)*, **5**, 868 (1964).

(21) N. M. Emanuel, *Dokl. Akad. Nauk SSSR*, **45**, 603 (1954).

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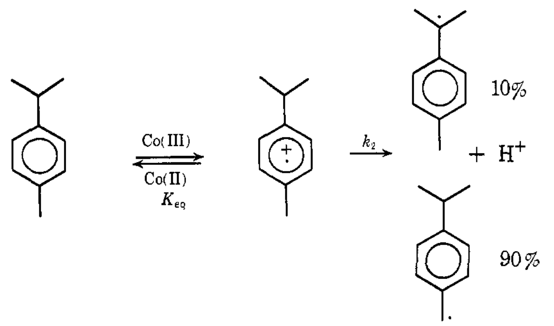
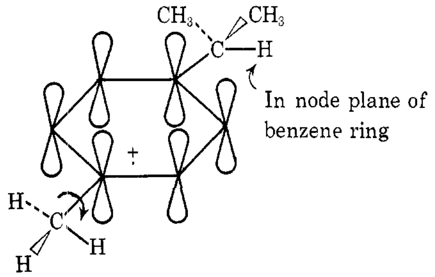


In the preferred geometry, the tertiary hydrogen on the isopropyl group of *p*-cymene is located in the node plane of the benzene ring where its interaction with the π system in the transition state is minimized. The methyl group, on the other hand, rotates freely and is therefore affected preferentially. Recent esr data support the proposed orientation of alkyl groups in radical cations on the basis of R values[26] (ratio of β-proton coupling constant to the corresponding methyl proton coupling constant: R = 0.3 for isopropyl, no rotation; 1.0 for ethyl, free rotation at 25°). Such remarkable selectivity prevails during the oxidation of *p*-cymene and *sec*-butyltoluenes, and to a lesser extent in *p*-ethyltoluene.



Precisely what is involved, induction, hyperconjugation, solvation, mass effects, or any combination of the factors, lies beyond the scope of this paper. Benzyl radicals add oxygen to afford peroxy radicals which then may terminate in several different ways which do not necessarily proceed through a hydroperoxide stage. Some of these possibilities have been recently discussed.[27] In the absence of detailed kinetic data, it is difficult to predict which of the proposed possibilities, if any, are applicable under our experimental conditions.

Experimental Section

Apparatus and Materials.—Oxidations were carried out in a 1-l., 316 stainless steel, magnetically stirred autoclave (Autoclave Engineers, Inc., Erie, Pa.) at 105° and 22 atm of total pressure. The autoclave was equipped with a cooling coil and heaters, and was connected to an oxygen supply system, temperature and pressure controllers, and recording instruments. Complete conversion of aromatics was obtained in most experiments, whereas recovery of products was usually 95% or better. The nmr spectra were obtained on a Varian T-60 spectrometer (DMSO-d_6, TMS). Chemical shifts are in δ units, in parts per million. The ir spectra were recorded either on Perkin-Elmer Infracord or Model 237B spectrometers. Carboxylic acids were analyzed by vapor phase chromatography (vpc) as trimethylsilyl derivatives (4 ft × 0.25 in. OV-1 column, programmed from 50 to 250° at 10°/min).

p-Cymene and *p*-ethyltoluene were purchased from Chemical Samples Co., Columbus, Ohio (minimum purity of 99+%), and were used as received. *sec*-Butyltoluenes, bp 193–198°, and other hydrocarbons were obtained from this laboratory.

Oxidation of *p*-Cymene.—A mixture consisting of 20 g of $Co(OAc)_2 \cdot 4H_2O$, 20 g of MEK, and 53 g (0.39 mol) of *p*-cymene in 400 g of glacial acetic acid was charged into the autoclave. After addition of 70 g of *n*-butane by means of Milroy pump, the autoclave was pressured with oxygen to 10 atm and heated to 105°. Additional oxygen was introduced to bring the pressure inside the autoclave to 22 atm. After an induction period of 1 hr, reaction was continued for 1.5 hr. The autoclave was cooled and depressured, and the product mixture was removed. The low-boiling components were removed under reduced pressure in a rotary evaporator, and 500 ml of ice water was added to the residue. The white precipitate that formed was filtered, washed with water, and dried in a vacuum oven to give 65 g of solids. Analysis of product by vpc and nmr indicated the product to be a mixture of *p*-isopropylbenzoic acid (90%) and *p*-acetobenzoic acid (10%). This result was confirmed by vpc by doping with standards. Repeated crystallization of crude material from aqueous acetic acid gave pure *p*-isopropylbenzoic acid: mp 114–116° (lit.[28] mp 116–117°); nmr δ 1.26 (d, 6, CH_3), 2.95 (m, 1, CH), 7.29 (d, 2, ring), and 7.9 (d, 2, ring). A portion of isolated *p*-acetobenzoic acid melted at 203–206° (lit.[29] mp 208°), nmr δ 2.64 (s, 3, CH_3) and 8.1 (s, 4, ring).

Oxidation of *p*-Ethyltoluene.—Oxidation of ethyltoluene was carried out in a manner described for *p*-cymene. Experimental conditions and results obtained are summarized in Table I. On work-up, 16 g (68%) of *p*-ethylbenzoic acid was isolated: mp 108–110° (lit.[30] mp 113.5°); nmr δ 1.2 (t, 3, CH_3), 2.6 (q, 2, CH_2), 7.25 (d, 2, ring), and 7.88 (d, 2, ring). In addition, the acid fraction also contained 0.7 g (2%) of *p*-acetobenzoic acid, 1.3 g (5.5%) of *p*-toluic acid, and a trace of terephthalic acid (all by vpc). The neutral fraction contained 5.5 g (25%) of *p*-methylacetophenone, whose ir spectrum and relative retention time were identical with those of an authentic sample.

Oxidation of *sec*-Butyltoluenes.—Starting with 62 g of *sec*-butyltoluenes, a total of 66 g (89%) of the corresponding carboxylic acids were obtained, neutral equivalent of 175. The ratio of ring protons to that on the alkyl group by nmr was 4:9, consistent with *sec*-butylbenzoic acids. Isomeric distribution of charge and product were determined by vpc. Results are included in Table I.

Competitive Rate Study.—Competitive oxidations on mixtures of substrates were done under conditions earlier described for *p*-cymene. Results are shown in Table III. The initial concentration of each substrate was held at low value (~0.1 *M*) to minimize possible solvent effects. After the initiation period was over, reaction was allowed to proceed for 5 min. The initial charge and the pentane extract of the final mixture were analyzed directly by vpc for the disappearance of starting hydrocarbons. Analyses were carried out (Varian 1520 chromatograph, TC detector) on two columns using *tert*-butylbenzene as internal standard: 20 ft × $^1/_8$ in., 5% Bentone 24 and DC 200 on Chrom W at 95°, and 20 ft × $^1/_4$ in., 20% β,β'-oxydipropionitrile on Chrom W at 100°. All reactivities were related to toluene using the following expression

$$\frac{k_a}{k_b} = \frac{\log([A]_f/[A]_i)}{\log([B]_f/[B]_i)}$$

where A and B refer to concentrations of the two substrates before and after the reaction.

Registry No.—Cobaltic ion, 22541-63-5; *p*-cymene, 99-87-6; *p*-ethyltoluene, 622-96-8; *sec*-butyltoluenes, 26571-04-0.

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