allowed to cool to −20° (CCl_4 + Dry Ice bath). Five millimoles of benzoic acid dissolved in 2.5 ml of THF (cooled to −20°) was then added slowly under vigorous stirring. After 10 min the mixture was heated up and kept under reflux. After different time intervals the mixture was cooled to 0° and 5-ml aliquots were withdrawn and analyzed for aldehyde. After 12 hr 0.197 g of 2,4-DNP derivative was obtained (70%); after 24 hr 0.232 g (82%) was obtained; and this remained constant after 36 hr. From caproic acid, using the same procedure as from benzoic acid, a 68% yield after 12 hr, 88% yield after 24 hr, and 98% yield after 36 hr were realized.

Registry No.—Thexylborane, 3688-24-2; diborane, 13283-31-3; disiamylborane, 1069-54-1.

Nonclassical Oxidation of Aromatics. II. Cobaltic Ion Catalyzed Oxidations of 1,1-Di(*p*-tolyl)ethane and 1,1-Di(3,4-dimethylphenyl)ethane

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Co^{III} ion catalyzed oxidation with oxygen in acetic acid has been extended to the 1,1-diarylalkanes. Major and novel products are carboxylic acids in which the bridging ethylidene group survives the oxidation. 1,1-Di(*p*-tolyl)ethane gave 1,1-di(4-carboxyphenyl)ethane (70%) as the major product. 1,1-Di(3,4-dimethylphenyl)ethane afforded isomeric dimethyl, dicarboxylic acids (85%). The products of this oxidation are unexpected, assuming a free-radical pathway. An electron transfer mechanism involving radical cation intermediates is therefore proposed.

Inorganic oxidants including chromic acid, potassium permanganate, and nitric acid are known to oxidize 1,1-diarylalkanes to benzophenone polycarboxylic acids.[1-3] Air oxidation, however, has been limited to di(*p*-tolyl)methane[4,5] and 2,2-diarylalkanes.[6,7] Di(*p*-tolyl)methane was oxidized to a benzophenone dicarboxylic acid. Attempts to oxidize 1,1-di(*p*-tolyl)ethane or 1,1-di-(3,4-dimethylphenyl)ethane with oxygen in the liquid phase led to low conversion of almost exclusively nonacidic oxidation products.[8] Similar difficulties were encountered in the attempted oxidation of alkoxytoluenes in acetic acid.[9] In these cases, initially formed hydroperoxide cleaves into phenolic materials which then terminate the reaction. A recent paper describes the synthesis of 1,1-di(*p*-tolyl)ethyl hydroperoxide and its subsequent cleavage to form *p*-cresol and *p*-methylacetophenone.[10]

We have proposed an electron transfer mechanism for the selective oxidation of alkyltoluenes in which methyl groups are preferentially attacked.[11] Extending this work, liquid phase oxidation of 1,1-di(*p*-tolyl)ethane (DTE) and 1,1-di(3,4-dimethylphenyl)ethane (DXE) was examined.

Results

Oxidations were carried out in acetic acid using cobaltous acetate catalyst and methyl ethyl ketone (MEK)–butane as the promotors. Reactants, experimental conditions, and the results obtained are summarized in Table I.

Oxidation of DTE in the presence of cobaltous acetate without a promotor was slow, nonselective, and incomplete, even after 20 hr (expt 1). A mixture of monoacids, including 1-(4-carboxyphenyl)-1-(4-methylphenyl)ethane (I) and 4-methyl-4′-carboxybenzophenone, was isolated (21%) along with 4,4′-dimethylbenzophenone (26%). A similar experiment, but with MEK, afforded I in 45.4% yield (expt 2). Oxidation of DTE in the presence of MEK–butane gave 1,1-di(4-carboxyphenyl)ethane (EDB) and I in yields of 67.3 and 8.3%, respectively (expt 3). Extension of the reaction time beyond a 5–6-hr period did not improve the yields of I or EDB significantly.

Oxidation of DXE under conditions used for DTE gave an isomeric mixture of the corresponding ethylidenedi- and -monocarboxylic acids exclusively (expt 5).

Recovery of products in all experiments was above 85%, whereas cleavage into fragments was between 5 to 10%. Cleavage products from DTE oxidation were (vpc) *p*-acetobenzoic acid, *p*-toluic acid, terephthalic acid, some *p*-methylacetophenone, and traces of *p*-cresol.

Discussion

Oxidation of 1,1-di(*p*-tolyl)ethane and 1,1-di(3,4-dimethylphenyl)ethane in the system earlier described for alkyltoluenes was investigated.[11] Major and novel products are carboxylic acids in which the bridging ethylidene group remains intact. Large amounts of catalyst in the higher valency state were required to effect selective methyl group oxidation. With Co^{II} ions alone, reaction did not proceed readily and showed no selectivity. Peroxy radicals derived from the substrate were apparently not sufficient to maintain the active Co^{III} species. If the overall rate of reaction is

$$RO_2\cdot + Co^{II} \longrightarrow R'CHO + Co^{III} + OH^-$$

governed by the reoxidation of Co^{II} to Co^{III}, it should be helped by peroxy radical-forming promoters. Adding for this purpose MEK or cyclohexanone showed an increase in rate and shortening of the induction period. As methylenic ketones are rapidly consumed, precursor

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[3] U. S. Patent 2,848,486 (1958).

[4] U. S. Patent 2,806,059 (1957).

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[7] U. S. Patent 3,161,693 (1964).

[8] U. S. Patent 3,424,789 (1969).

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[11] A. Onopchenko, J. G. D. Schulz, and R. Seekircher, *J. Org. Chem.*, **37**, 1414 (1972).

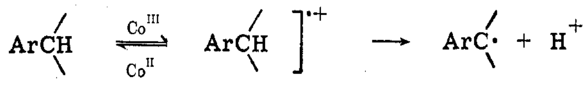
TABLE I

Expt no.	1	2	3	4	5
Reactants, g					
$Co(OAc)_2 \cdot 4H_2O$	21.5	20	20	31.5	20
MEK		15	15	20	30
HOAc	403	400	400	535	460
n-Butane			105	45	18
Substrate	DTE (38.8)	DTE (48.8)	DTE (52.5)	DTE (37.5)	DXE (84.0)
Conditions					
Temp, °C	105	105	105	118	105
Total pressure, atm[c]	24	28	20	26	20
Reaction time, hr	20	4.5	17	5.5	22
Product data, g (% yield)[d]					
I	9.4 (21)[a]	25.1 (45.4)	4.9 (8.3)	1.8 (4.3)	
II			45.3 (67.3)	35.2 (73)	
4,4′-Dimethylbenzophenone	10.5 (26)				
Dimethyldicarboxylic acids					52 (50%)[b]
Trimethylcarboxylic acids					23 (25)
Methyltricarboxylic acids					Trace

[a] *Ca.* a 50:50 mixture of I and 4-methyl-4′-carboxybenzophenone. [b] Continued reaction for 6 hr with added butane; yield, 85%. [c] Mostly partial pressures of butane and oxygen. [d] Based on aromatic feed.

hydrocarbons such as *n*-butane and cyclohexane were used as promotors of greater permanency.

Products obtained were not expected from a normal free-radical pathway. By this mechanism, hydrogen on the bridging ethylidene group would have been preferentially abstracted.[12] That simple radical abstraction was not involved is shown by the different nature of the products formed, the dependence of the reaction rate on catalyst concentration,[11] and the relative reactivities of different substrates toward Co^{III} ions (Table II). Most striking is the inertness of the benzylic tertiary hydrogens. This has been observed in electrophilic chlorination and diazotizations[13] for systems in which a positive charge is developed either at or adjacent to an aromatic ring. Sakota, *et al.*,[14] rationalized this observation in terms of an entropy decrease of the substrate in the transition state. Lack of available σ^+ values for our compounds prevented us from obtaining a reliable ρ value. The data show, however, that electron-withdrawing substituents retard oxidation in this system. Consistent with a positively charged transition state is an anticipated negative ρ value. The following mechanism for 1,1-diarylalkanes oxidation would agree with our line of reasoning. Loss of proton appears to be controlled by stereoelectronic factors rather than the thermodynamic stability of the product. Results are therefore best rationalized by path a. To account for this unusual selectivity, a steric configuration is proposed with tertiary hydrogen located in the node plane of the benzene ring, where any action upon it in the transition state would be minimized. This is supported by recent esr studies which show that groups such as isopropyl exhibit no free rotation in radical cations when compared to methyl or ethyl.[15]



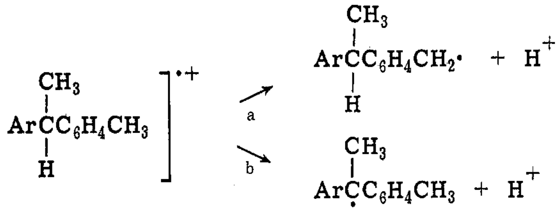


TABLE II

RELATIVE REACTIVITIES OF AROMATICS TOWARD COBALTIC ION[a]

	Reactivity per molecule	Reactivity/ methyl group
1,1-Di(*p*-tolyl)ethane	12	(6.0)[c]
1,1-Di(3,4-dimethylphenyl)ethane	23	(5.8)[c]
p-Cymene	2.4	(2.4)[c,d]
Toluene	1.00[b,f]	1.00[b]
Diphenylmethane	0.5[e]	
3,4,3′,4′-Tetramethylbenzophenone	1.6	0.4
4,4′-Dimethylbenzophenone	0.6	0.3
p-Tolyl sulfone	0.6	0.3
3,4-Dimethylphenyl sulfone	0.8	0.2
4,4′-Dimethylbiphenyl	0.3	0.15
Triphenylmethane	0.2[e]	
Cumene	0.1[f]	
Phenyl ether	0.0[g]	

[a] 100°, 22-atm total pressure, in presence of MEK–C_4H_{10}. [b] Assumed standard, reactivity = 1.00. [c] Assumed negligible contribution from reactivity of the tertiary hydrogen, based on low reactivity of cumene and triphenylmethane. [d] 90% of the reaction was at the methyl group.[11] [e] 40°, from Table I of ref 14. [f] Our values agree with those of footnote *e*. [g] Internal standard.

Benzyl radicals produced are trapped by oxygen to give peroxy radicals which then terminate. Termination of such radicals can occur through various pathways which do not necessarily proceed *via* a hydroperoxide route.[16] In the absence of kinetic data we do not wish to speculate on the mechanism of termination.

During more recent work with aliphatic substrates in the same system, rates and general characteristics of this type of oxidation were almost identical with those with the alkyltoluenes and diarylalkanes. Formation of radical cations is therefore not a prerequisite for

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(15) D. H. Geske, *Progr. Phys. Org. Chem.*, **4**, 125 (1967).

(16) C. Walling, *J. Amer. Chem. Soc.*, **91**, 7590 (1969).

electron transfer, but rather an accompanying phenomenon in aromatic systems.

Experimental Section

Apparatus and Materials.—Oxidations were carried out in a 1-l., 316 stainless steel, magnetically stirred autoclave (Autoclave Engineers, Inc., Erie, Pa.) under conditions described in Table I. The autoclave was equipped with a cooling coil and a heating mantle, and was connected to an oxygen supply system, temperature and pressure controllers, and recording instruments.

The nmr spectra were obtained on a Varian T-60 spectrometer (solvent, TMS). Chemical shifts are in δ units, parts per million. The ir spectra were recorded either on Perkin-Elmer Infracord or Model 237B spectrometers. The products 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).

All aromatic hydrocarbons used in our work were available in this laboratory or prepared by standard procedures.

Oxidation of DTE.—A typical procedure used for the oxidation of diarylalkanes is described for DTE (expt 4). A mixture of 31.5 g of cobaltous acetate tetrahydrate, 525 g of acetic acid, 20 g of MEK, 37.5 g (0.178 mol) of DTE, and 45 g of *n*-butane was placed into the autoclave. The autoclave was pressured with oxygen to ~10 atm, and heated to 118°. Additional oxygen was introduced to bring the pressure inside the autoclave to 26 atm. After an induction period of 1 hr, the reaction was continued for 5.5 hr. The autoclave was cooled and depressured, and the product mixture was removed.

Filtration of crude product afforded 25 g of solids (first crop). The filtrate was evaporated to dryness on a rotary evaporator, and the residue was extracted with acetone to afford a second crop of solids. The acetone insoluble material, mostly catalyst, was treated with concentrated hydrochloric acid and filtered to afford a third crop of solids. The combined solids were washed with water and then dried (vacuum oven) to give 44 g of product. Analysis by vpc had indicated that 35.2 g (0.13 mol, 73%) of EDB, and 1.6 g (0.007 mol, 4.3%) of I were present in the mixture. About 6.6 g of material consisted of *p*-toluic acid, *p*-methylacetophenone, *p*-acetobenzoic acid, a trace of 4,4-dimethylbenzophenone and terephthalic acid, and unknowns. The entire product was dissolved in acetone from which EDB was obtained by repeated crystallization [mp 278° (lit.[17] mp 280°); ir $\nu_{\mathrm{COOH}}^{\mathrm{Nujol}}$ 1695 (s), ν_{ring} 1610 cm^{-1}], present in benzoates but not in terephthalates or benzophenones: nmr ($Cl_2HCCOOH$, TMS) 8.0 (d, 4, ring), 7.3 (d, 4, ring), 4.3 (q, 1, =CH–), and 1.72 (d, 3, CH_3).

Anal. Calcd for $C_{16}H_{14}O_4$: C, 71.1; H, 5.22. Found: C, 70.8; H, 5.3; neut equiv, 135.5.

Isolation of I.—Oxidation of 48.8 g of DTE (expt 2) for 4.5 hr afforded a partially oxidized product. The solvents were removed on a rotary evaporator and the residue was treated with aqueous sodium hydroxide to precipitate the catalyst. After filtering, the filtrate was acidified with hydrochloric acid to give 36 g of acids. Analysis by vpc indicated 25.1 g (0.1 mol, 45.4%) of I to be in the mixture. A 10-g sample of crude product was purified by base-acid treatment and recrystallized from aqueous methanol to give 5.6 g of I: mp 95–8°; ir $\nu_{\mathrm{COOH}}^{\mathrm{Nujol}}$ 1695 (s), ν_{ring} 1610 cm^{-1} (m); nmr (acetone-d_6, TMS) 7.0 (s, 4, ring), 7.25 (d, 2, ring), 7.9 (d, 2, ring), 4.11 (q, 1, =CH–), 2.27 (s, 3, CH_3), and 1.61 (d, 3, CH_3CH=).

Anal. Calcd for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 80.2; H, 6.9; neut equiv, 241.6.

Oxidation of DXE.—Oxidation of DXE (expt 5) was carried out under conditions used for DTE. At the end of this experiment, a sample of product mixture was withdrawn and analyzed by vpc (internal standard method). Analysis indicated that 52 g (50%) of dicarboxylic acids and 23 g (24.5) of monocarboxylic acids were formed. Continued oxidation of mixture in the presence of added butane afforded dicarboxylic acids predominantly (85%). Neutral equivalent determination and the nmr data were consistent with the vpc analysis. The absence of benzophenone derivatives was shown by the absence of the 1650 band in the infrared spectrum.

Competitive Rate Study.—Competitive rate study on mixtures of substrates was done under conditions used for oxidation of DTE alone. The initial concentration of each substrate in a mixture was held at a low value (~0.1 *M*).

The mixture was analyzed directly before and after the reaction for the disappearance of starting substrates (vpc, internal standard method). In addition to OV-1 column, 20 ft × $^1/_8$ in., 5% Bentone 24 and DC 200 on Chrom W was also used at 95°. All reactivities were related to toluene, assumed reactivity = 1.00, by the following expression, where subscripts refer to final and initial concentrations (wt %).

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

Registry No.—I, 35026-55-2; DTE, 530-45-0; DXE, 1742-14-9; EDB, 35026-58-5; Co^{III} ion, 22541-63-5.

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[17] A. Haiss, *Ber.*, **15**, 1481 (1882).