in. SE-30/Chromosorb P and found to contain 4 (0.6%, retention time 9 min), 31 (1.6%, retention time 7 min) and 32 (17.4%), retention time 23 min).

31: white solid, mp 74–76° (from hexane); ir (CHCl₃, μ) 6.23, 11.0, 15.5; nmr (CDCl₃, δ) 7.4 (5 H, s), 6.6 (1 H, d of t, $J = 2, 7$ Hz), 6.2–6.0 (4 H, m), 5.5 (1 H, d, $J = 11$ Hz), 4.4 (1 H, m), 3.4 (1 H, m); mass m/e 206 (M⁺); uv λ_{max}^{MeOH} 265 (log ε 4.100). Anal. Calcd for C₁₆H₁₄: C, 93.16; H, 6.84. Found: C, 92.77; H, 7.08.

32: ir (CHCl₃, μ) 6.24, 11.9, 14.5; nmr (CDCl₃, δ) 7.3 (5 H, s), 5.8–6.7 (5 H, m), 4.5 (1 H, m), 3.58 (1 H, m), 2.5–3.3 (3 H, m); mass m/e 244, 242 (ratio 1:3, M⁺); uv λ_{max}^{MeOH} 285 (log ε 4.198).

Potassium *tert*-Butoxide Treatment of 32. 32 (0.022 g, 0.97 mmol) in ether (1 ml) was added to a rapidly stirred solution of potassium *tert*-butoxide (0.017 g, 0.15 mmol) in dimethyl sulfoxide (1 ml). After the mixture was stirred for 1 hr, water (5 ml) was added and the resulting solution extracted with pentane (4 × 15 ml). The pentene layers were combined, dried (MgSO₄), and filtered, and the solvent was evaporated *in vacuo.* Glpc analysis (see above) indicated a 60% conversion to 4.

9-Benzylidenebicyclo[4.2.1]nona-2,4,7-triene (30). The procedure for the synthesis of 4 (see above) was followed with bicyclo[4.2.1]-nona-2,4,7-trien-9-one[23] (80 mg, 0.6 mmol). Plc with hexane yielded 30 (R_f 0.4, 56 mg, 62%) which could be recrystallized from hexane: mp 76–77°; ir (CHCl₃, μ) 6.5, 14.6, 15.2; nmr (CDCl₃, δ) 7.2 (5 H, s), 5.8–6.4 (5 H, m), 5.35 (2 H, m), 3.75 (1 H, d, $J = 7$ Hz), 3.5 (1 H, d, $J = 7$ Hz); uv λ_{max}^{MeOH} 245 (log ε 4.36), 270 (4.059); mass m/e 206 (M⁺).

4-Benzylidenebicyclo[3.2.2]nona-2,6,8-triene (31). The procedure for the synthesis of 4 (see above) was followed with bicyclo[3.2.2]-nona-2,6,8-trien-4-one[24] (0.200 g, 1.5 mmol). Plc with hexane yielded 31 (R_f 0.4, 48 mg, 17%).

Hydration of Bullvalene 1. Sulfuric acid (10%, 90 ml) was added to a rapidly stirred solution of 1 (1.292 g, 9.75 mmol) in THF (75 ml). The mixture was heated to 54° and stirred for 34 hr. After cooling to room temperature, the reaction was neutralized with saturated Na₂CO₃ solution and extracted with pentane (4 × 50 ml). The aqueous phase was saturated with NaCl and washed with ether (3 × 50 ml). The combined organic solutions were dried (MgSO₄), filtered, and concentrated *in vacuo.* Plc with 10% acetone and 10% chloroform in hexane (eight developments) yielded 36 (R_f 0.4, 0.662 g, 46%). 36 was recrystallized from

hexane: mp 49.5–50.5°; ir (CHCl₃, μ) 2.9, 6.1; nmr (CDCl₃, δ) 1.1–2.7 (6 H, m), 4.1–4.7 (2 H, m), 5.5–6.3 (4 H, m). Anal. Calcd for C₁₀H₁₂O: C, 81.04; H, 8.16. Found: C, 81.08; H, 8.27.

Tricyclo[4.3.1.0²,⁹]deca-3,7-dien-10-one. To 36 (0.083 g, 0.56 mmol) in ether (10 ml) was added active MnO₂ (0.8 g). After 14 hr of stirring at room temperature, the mixture was filtered and the ether solution concentrated using a 6-in. Vigreux column. Plc with chloroform yielded tricyclo[4.3.1.0²,⁹]deca-3,7-dien-10-one (R_f 0.5, 0.041 g, 50%): mp 32°; ir (CHCl₃, μ) 3.3, 5.93; nmr (CDCl₃ δ) 2.15–2.5 (5 H, m), 2.9–3.15 (1 H, m), 5.8–6.1 (4 H, m); uv λ_{max}^{MeOH} 208 (ε 3460). Anal. Calcd for C₁₀H₁₀O: C, 82.16; H, 6.89. Found: C, 82.17; H, 6.73.

Tricyclo[4.3.1.0²,⁹]decan-10-one (38) by Catalytic Hydrogenation. Tricyclo[4.3.1.0²,⁹]deca-3,7-dien-10-one (0.020 g, 0.14 mmol) was dissolved in ethyl acetate (3 ml) containing platinum oxide (20 mg) in an atmospheric hydrogenation flask (10 ml). After 2 equiv of hydrogen gas was taken up (6.1 ml, 15 min), the reaction was filtered and the solvent concentrated *in vacuo.* The residue was separated by plc with chloroform to yield 38 (R_f 0.65, 0.008 g, 38%): ir (CHCl₃, μ) 6.0; nmr (CDCl₃, δ) 1.3–2.2 (12 H, m), 2.5–2.7 (2 H, m); exact mass for C₁₀H₁₄O, 150.10427 (calcd, 150.10439).

Diazo Ketone 37. Cyclooct-4-ene carbonyl chloride[31] (3.9 g, 22.6 mmol) in ether (10 ml) was added to a solution of diazomethane (from 21.5 g of Aldrich Diazald) in ether (100 ml) at 0°. After 2 hr stirring, the solution was warmed to room temperature and the ether and excess diazomethane were blown off using a stream of nitrogen to yield 37 (4.0 g, 97%): ir (CHCl₃, μ) 4.75, 6.15; nmr (CDCl₃, δ) 5.5–5.8 (2 H, m), 5.2 (1 H, s), 1.2–2.9 (11 H, m).

Tricyclo[4.3.1.0²,⁹]decan-10-one (38) from 37. 37 (0.692 g, 4.4 mmol) in dry cyclohexane (15 ml) was added over 1 hr to a re-fluxing, rapidly stirred mixture of anhydrous copper sulfate (0.2 g) and cyclohexane (70 ml). After the addition was complete, the reaction was allowed to stir an additional hour, then cooled to room temperature, and filtered, and the solvent was concentrated *in vacuo.* The residue was separated by plc with 10% acetone in hexane eluent to yield 38 (R_f 0.3, 0.138 g, 24%).

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Oxidation of Organic Compounds with Cerium(IV). XVII.[1] Oxidation of 1,2-Diarylethanes

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Abstract: The oxidation of 1,2-diarylethanes by ceric ammonium nitrate in 70% aqueous acetonitrile containing nitric acid (0.36 M) at 80° was found to produce cleavage products only, substituted benzaldehydes, benzyl nitrates, and benzyl alcohols. The relative rates of oxidation of 1,2-diphenylethane, 1-*p*-tolyl-2-phenylethane, 1,2-di-*p*-tolylethane, 1,2-di-*p*-chlorophenylethane, 1,2-di-*m*-chlorophenylethane, and 2,3-diphenyl-2,3-dimethylbutane were found to be 1.00, 30.0, 68.2, 0.292, 0.0415, and 5.39, respectively, by competition studies. A mechanism is proposed which involves the rate-limiting formation of radical cation intermediates which is followed by cleavage of the central carbon–carbon bond of these radical cations to produce a benzyl radical and benzyl cation.

In previous studies of the metal ion oxidations of alkylarenes, mechanisms have been postulated which

involve benzyl radicals generated by α-hydrogen atom abstraction[2–5] or radical cation intermediates generated by electron transfer from the π-electron system

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**Table I.** Absolute Yields of Products from the CAN Oxidation of 1,2-Diarylethanes[a]

1,2-Diarylethane, mmol	CAN mmol	Yield, mmol[b]		
		ArCHO	ArCH$_2$OH	ArCH$_2$ONO$_2$
$(C_6H_5CH_2-)_2$ (2.2)	8.0	1.36 ± 0.07	0.08 ± 0.03	0.88 ± 0.66
$(p\text{-}CH_3OC_6H_5CH_2-)_2$ (2.1)	8.0	2.45 ± 0.02	0.50 ± 0.01	0.03 ± 0.01
$(p\text{-}CH_3C_6H_5CH_2-)_2$ (1.9)	10.0	1.91 ± 0.03	0.44 ± 0.02	0.23 ± 0.02

[a] In 70% aqueous acetonitrile containing nitric acid (0.36 M) at 80°. [b] All yields are determined by nmr on unpurified products and are based on at least two runs; diphenylmethane was used as a standard.

of the arene.[5–10] We have studied the ceric ammonium nitrate (CAN) oxidation of 1,2-diarylethanes and wish to present evidence which supports the rate-limiting formation of radical cation intermediates which is followed by cleavage of the central carbon–carbon bond of these radical cations to produce a benzyl radical and benzyl cation.

Results and Discussion

The CAN oxidation of 1,2-diarylethanes in 70% aqueous acetonitrile containing nitric acid (0.36 M) at 80° gives only products derived from cleavage of the central carbon–carbon bond. The yields of the products

$$ArCH_2CH_2Ar \xrightarrow{4CAN\ (0.16\ M)} \begin{array}{l} ArCH_2ONO_2 \\ ArCH_2OH \\ ArCH=O \end{array}$$
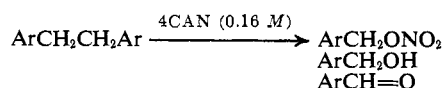
obtained from the oxidation of 1,2-diphenylethane (1), 1,2-di-p-methoxyphenylethane (2), and 1,2-di-p-tolylethane (3) are present in Table I. Possible mechanisms for the oxidation of an unsymmetrical 1,2-diarylethane are shown in Scheme I.

Scheme I
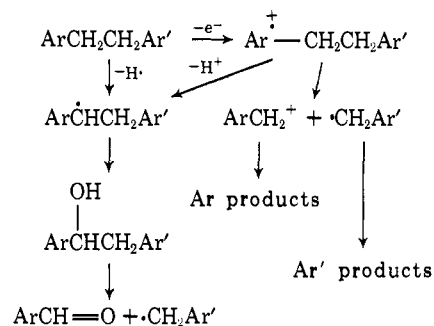
A competitive CAN oxidation of 1 and 2,3-diphenyl-2,3-dimethylbutane (4) was carried out in 70% aqueous acetonitrile containing nitric acid (0.36 M) at 80°. From the amounts of starting hydrocarbons in the product mixtures it was calculated that the tetramethyl compound is oxidized 5.39 ± 0.76 times faster than the parent system. Since 4 has no α-hydrogen atoms, α-hydrogen atom abstraction cannot be involved in its oxidation. The comparable rates of oxidation of 1 and 4 are consistent with α-hydrogen atom abstraction being unimportant in the oxidation of 1 also.

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In contrast to these results, α-hydrogen atom abstraction has been established as the rate-determining process for the chromium(VI) oxidation of alkylarenes[11] and it has been shown that 4 is oxidized slowly by chromium(VI).[12] Also, the k_H/k_D = 1.8 for the cerium(IV) oxidation of toluene and toluene-α,α,α-d_3 in acetic acid[13] is much smaller than the k_H/k_D = 6.4 found for the chromium(VI) oxidation of diphenylmethane and diphenylmethane-α,α-d_2.[11] This suggests that the mechanism for the cerium(IV) oxidation of alkylarenes is different from that for chromium(VI). Since the isotope effect of 1.8 is higher than that expected for electron-transfer only, possibly the rate-limiting step of the cerium(IV) oxidation of toluene consists of an electron-transfer reaction accompanied by α-proton loss.[14]

The relative rates of oxidation of several diarylethanes were measured by competition studies and are presented in Table II. If cleavage of the central carbon–carbon

Table II. Relative Rates of the Oxidation of 1,2-Diarylethanes by CAN[a]

Compd	k_{rel}
$(C_6H_5CH_2-)_2$ (1)	1.00
$p\text{-}CH_3C_6H_4CH_2CH_2C_6H_5$ (5)	30.0 ± 0.14
$(p\text{-}CH_3C_6H_4CH_2-)_2$ (3)	68.2 ± 0.60
$(p\text{-}ClC_6H_4CH_2-)_2$ (6)	0.292 ± 0.04
$(m\text{-}ClC_6H_4CH_2-)_2$ (7)	0.0415 ± 0.005

[a] In 70% aqueous acetonitrile containing nitric acid (0.36 M) at 80°; concentration of each $(ArCH_2-)_2$ was 0.04 M; [CAN] = 0.2 M.

bond is the rate-determining process, the rate increase in going from the monomethyl to the dimethyl hydrocarbon should be about the same as that found in going from the parent system to the monomethyl compound since both aromatic rings would be directly attached to the bond which is cleaving in the transition state. If, however, radical cation formation is the rate-determining process, the dimethyl compound should be oxidized only about twice as fast as the monomethyl compound since there would be two sites for radical cation formation instead of one. The results presented in Table II are more consistent with the formation of a radical cation in the rate-determining process than with cleavage of the central carbon–carbon bond since the rate of oxidation of 3 is approximately twice that of 5, not 30 times greater which is the relative rate of oxidation of 5 compared to 1.

The radical cation could undergo cleavage of the

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central carbon–carbon bond to generate a benzyl radical and benzyl cation or lose a proton from the α position to generate a 1,2-diarylethyl radical. This radical would be oxidized to the cation by cerium(IV) which could then react with water to yield a 1,2-diaryl-ethanol which would be further oxidized by cerium(IV) to generate the observed products. Oxidative cleavage of 1,2-diarylethanols would occur rapidly under these conditions.[15]

α-Hydrogen atom abstraction is not favored since **4** is easily oxidized, but if formation of the 1,2-diaryl-ethanol is operative, only 1-p-tolyl-2-phenylethanol would be an intermediate in the oxidation of **5** since the large relative rate of oxidation of **5** compared to **1** indicates formation of the radical cation only at the p-tolyl group. Oxidation of 1-p-tolyl-2-phenylethanol would give rise to p-tolualdehyde, benzyl nitrate, benzyl alcohol, and benzaldehyde only, no p-methylbenzyl alcohol or nitrate.[15] However, if the intermediate radical cation undergoes cleavage of the central carbon–carbon bond to produce a benzyl radical and benzyl cation, then all possible products could be formed. Analysis of the product mixture from the oxidation of **5** showed that all possible products were formed: p-tolualdehyde (63%), benzaldehyde (20%), p-methyl-benzyl alcohol (5%), benzyl alcohol (7%), p-methyl-benzyl nitrate (10%), and benzyl nitrate (43%). Thus, the intermediate radical cation must undergo fragmenta-tion to give the benzyl radical and benzyl cation.

A Hammett σ plot of the rate data given in Table II vs. σ^+ values[16] gave a ρ of -4.61 ± 0.43. The relative rate constant for **5** was multiplied by 2 since **5** has only one activated aromatic ring. This ρ value is much larger in a negative sense than the value of -2.4 ob-tained for the cobalt(III) oxidation of toluenes[6b] which is thought to involve an electron-transfer mechanism.[17]

This mechanism for the CAN oxidation of 1,2-diarylethanes which involves the fragmentation of the radical cation of the 1,2-diarylethane is analogous to the mass spectral process for 1,2-diphenylethane[18] and is only the second analogy between mass spectrometry and solution phase oxidations[19] and the first example in-volving a metal ion oxidant.

Experimental Section

Methods and Materials. Most equipment and general methods have been described previously.[1a] Glpc analyses were carried out using a 1 m × 6.25 m aluminum column packed with 20% SE-52 on Chromosorb W (80–100 mesh). Elemental analyses were carried out by Spang Microanalytical Laboratory, Ann Arbor, Mich. Bibenzyl (**1**) and diphenylmethane (distilled before use) were obtained from Aldrich Chemical Co. 2,3-Dimethyl-2,3-diphenylbutane (**4**) was obtained from Chemical Samples Co.

1,2-Di-p-methoxyphenylethane (2). To 3.5 g of magnesium in 50

ml of ether was added dropwise 25.5 g of 4-methoxybenzyl chloride (Aldrich) in 25 ml of ether. After the addition was complete, the mixture was stirred for 1 hr and then worked up to give a crude product which was chromatographed on alumina using hexane as an eluent to give 12.4 g (40%) of **2**: mp 125–126° (lit.[20] mp 125°); nmr (CDCl₃) δ 6.97 (m, 4), 6.67 (m, 4), 3.70 (s, 4), and 2.77 (s, 4).

1,2-Di-p-tolylethane (3) was prepared from 30 g of p-methyl-benzyl chloride (Aldrich) and 2.3 g of magnesium by the method used to prepare **2** except that after half of the benzyl chloride was added, the mixture was stirred for 1 hr and then the addition was completed and the mixture was stirred for 10 hr: yield, 10.1 g (22%); mp 83–84° (lit.[21] mp 81–82°); nmr (CCl₄) δ 6.98 (s, 8), 2.80 (s, 4), and 2.30 (s, 6).

1-p-Tolyl-2-phenylethane (5) was prepared by reduction of phenyl p-tolyl ketone[22] with hydrogen gas using 10% palladium on char-coal as the catalyst in 50% ethanol–ethyl acetate and purified by chromatography: yield 90%; mp 25° (lit.[23] mp 27°); nmr (CCl₄) δ 6.94 (s, 5), 6.85 (s, 4), 2.75 (s, 4), and 2.18 (s, 3).

1,2-Di-p-chlorophenylethane (6) was prepared from 32.2 g of p-chlorobenzyl chloride (Aldrich) and 2.6 g of magnesium by the method used to prepare **3** except that the mixture was stirred for 2 days. The crude product was purified by chromatography to give a 34% yield of **6**; mp 110–111° (lit.[24] mp 112°); nmr (CCl₄) δ 7.11 (m, 4), 6.89 (m, 4), and 2.80 (s, 4).

1,2-Di-m-chlorophenylethane (7) was prepared from 30 g of m-chlorobenzyl bromide (Aldrich) and 1.8 g of magnesium by the method used to prepare **3** except that the mixture was stirred for 24 hr. The crude product was purified by chromatography to give a 32% yield of **7**: mp 98–99°; nmr (CCl₄) δ 7.10 (m, 8) and 2.78 (s, 4); ir (CCl₄), 3045 (m), 2950 (m), 2860 (m), 1600 (s), 1480 (s), 1433 (s), 1090 (m), 1080 (m), 880 (m) 865 (m), and 695 (s) cm⁻¹; mass spectrum (70 eV) m/e (rel intensity) 254 (3), 252 (13), 250 (20), 128 (3), 127 (38), 126 (10), and 125 (100).

Anal. Calcd for C₁₄H₁₂Cl₂: C, 66.93; H, 4.82; Cl, 28.25. Found: C, 66.95; H, 4.77; Cl, 28.12.

Oxidation Procedure. The procedure used to oxidize **1** was typical. To 2.00 mmol of **1** in 40 ml of 70% aqueous acetonitrile containing nitric acid (0.36 M) was added 4.4 g of CAN in 10 ml of 70% aqueous acetonitrile. The reaction mixture was heated on a steam bath and allowed to reflux until the color of the solu-tion had faded to pale yellow. After the solution was cooled, standard (diphenylmethane) was added and the solution was poured into 50 ml of water. The mixture was extracted three times with 25 ml of ether. The combined ether extracts were washed three times with 10 ml of 1.2 M aqueous sodium hydroxide solution and three times with 25 ml of water, dried (MgSO₄), and concentrated on a rotary evaporator at reduced pressure. The residue was dissolved in CCl₄ and analyzed by nmr.

Competitive Oxidations. To 2.00 mmol of each diarylethane in 40 ml of 70% aqueous acetonitrile containing nitric acid (0.36 M) was added 5.5 g of CAN in 10 ml of the same solvent. The mix-ture was heated to reflux and allowed to reflux until the solution had faded to pale yellow. After the mixture was cooled, standard (diphenylmethane) was added and it was poured into 50 ml of water. The mixture was extracted three times with 25-ml por-tions of pentane, and the combined pentane extracts were washed three times with 10-ml portions of 1.2 M sodium hydroxide solution and one time with 25 ml of saturated sodium chloride solution, dried (MgSO₄), and concentrated under reduced pressure. In the competition between **1** and **4**, the residue was dissolved in carbon tetrachloride and analyzed by nmr. For the other competitions, the residue was dissolved in 5 ml of pentane and analyzed by glpc. Corrections for differences in extract ratios and thermal conduc-tivities were made. Relative constants were calculated as pre-viously described.[15]

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