239 ($M^+$); $^1H$ NMR $\delta$ 2.25 (s, 3 H), 7.20 (s, dd, 1 H, $J$ = 6 Hz, $J$ = 10 Hz), 7.70–8.20 (br s, 1 H), 8.20 (dd, 1 H, $J$ = 6 Hz, $J$ = 12 Hz); $^{19}F$ NMR $\phi$ 60.0 (s, 3 F), 115.0 (s, 1 F), 132.5 (s, 1 F). Anal. Calcd for $C_9H_6F_5NO$: C, 45.20; H, 6.05; N, 5.86. Found: C, 45.12; H, 2.52; N, 5.77. Compound **6b**: mp 117–119 °C; MS, $m/e$ 239 ($M^+$); $^1H$ NMR $\delta$ 2.25 (s, 3 H), 7.15–8.00 (m, 2 H), 8.20 (m, 1 H); $^{19}F$ NMR $\phi$ 60.5 (s, 3 F), 115.0 (s, 1 F), 134.5 (s, 1 F). Compound **6c**: mp 137–139 °C; MS, $m/e$ 239 ($M^+$); $^1H$ NMR $\delta$ 2.25 (s, 3 H), 6.90–7.50 (m, 3 H); $^{19}F$ NMR $\phi$ 56.0 (s, 3 F), 114.0 (s, 1 F), 134.5 (s, 1 F).

***N*-[3,5-Dichloro-4-(pentafluoroethyl)phenyl]acetamide (7a) and *N*-[3,5-Dichloro-2-(pentafluoroethyl)phenyl]acetamide (7b). Method B ($CHCl_3$/AcOEt, 20:1).** Compound **7a**: yield 22%; mp 163–164 °C; MS, $m/e$ 321; $^1H$ NMR ($CD_3OD$) $\delta$ 2.10 (s, 3 H), 7.70 (br s, 2 H); $^{19}F$ NMR $\phi$ 84.5 (s, 3 F), 105.0 (s, 2 F). Anal. Calcd for $C_{10}H_6Cl_2F_5NO$: C, 37.29; H, 1.88; N, 4.35. Found: C, 37.19; H, 1.77; N, 4.26. Compound **7b**: yield 27%; mp 154–157 °C; MS, $m/e$ 321; $^1H$ NMR ($CD_3OD$) $\delta$ 2.10 (s, 3 H), 7.05 (d, 1 H, $J$ = 2 Hz), 7.80 (d, 1 H, $J$ = 2 Hz); $^{19}F$ NMR $\phi$ 84.0 (s, 3 F), 104.0 (s, 2 F). Anal. Calcd for $C_{10}H_6Cl_2F_5NO$: C, 37.29; H, 1.88; N, 4.35. Found: C, 37.10; H, 1.65; N, 4.25.

**Isopropyl 5-Acetamido-4-fluoro-2-(trifluoromethyl)benzoate (8a) and Isopropyl 3-Acetamido-4-fluoro-2-(trifluoromethyl)benzoate (8b). Method B ($CHCl_3$).** Compound **8a**: yield 18%; mp 114–117 °C; MS, $m/e$ 303 ($M^+$); $^1H$ NMR $\delta$ 1.35 (d, 6 H), 2.25 (s, 3 H), 5.20 (q, 1 H, $J$ = 8 Hz), 7.40 (d, 1 H, $J$ = 11 Hz), 8.30–8.50 (br s, 1 H), 8.75 (d, 1 H, $J$ = 8 Hz); $^{19}F$ NMR $\phi$ 61.5 (s, 3 F). Anal. Calcd for $C_{13}H_{13}F_4NO_3$: C, 50.81; H, 4.26; N, 4.56. Found: C, 50.55; H, 4.11; N, 4.37. Compound **8b**: yield 15%; mp 98–100 °C; MS, $m/e$ 303 ($M^+$); $^1H$ NMR $\delta$ 1.35 (d, 6 H), 2.25 (s, 3 H), 5.20 (q, 1 H, $J$ = 8 Hz), 7.30–8.30 (m, 2 H), 7.90–8.20 (br s, 1 H); $^{19}F$ NMR $\phi$ 59.0 (s, 3 F).

**3,5-Bis(trifluoromethyl)-2-hydroxypyridine (9A). Method B**: yield 40%; mp 145.5 °C; MS, $m/e$ 231 ($M^+$); $^1H$ NMR $\delta$ 8.0 (br s); $^{19}F$ NMR $\phi$ 67.5 (s, 3 F), 63.5 (s, 3 F). Anal. Calcd for $C_7H_3F_6NO$: C, 36.38; H, 1.31; N, 6.06. Found: C, 36.09; H, 1.19; N, 6.05.

**2-Hydroxy-5-(trifluoromethyl)-3-(pentafluoroethyl)pyridine (9B). Method B**: yield 25%; mp 98.2 °C; MS, $m/e$ 281 ($M^+$); $^1H$ NMR $\delta$ 8.0 (br s); $^{19}F$ NMR $\phi$ 116.5 (s, 2 F), 84.0 (s, 3 F), 63.5 (s, 3 F). Anal. Calcd for $C_8H_3F_8NO$: C, 34.18; H, 1.07; N, 4.98. Found: C, 33.99; H, 1.03; N, 4.95.

**Methyl 5-(Heptafluoropropyl)-2-furancarboxylate (10). Method B**: yield 33%; oil; MS, $m/e$ 294; $^1H$ NMR $\delta$ 3.90 (3 H, t), 6.90 (1 H, m), 7.20 (1 H, m); $^{19}F$ NMR $\phi$ 128.0 (s, 2 F), 113.5 (m, 2 F), 81.5 (t, 3 F, $J$ = 8.3).

**3′,5′-Di-*O*-acetyl-5-(trifluoromethyl)-2′-deoxyuridine (11).** 3′,5′-Di-*O*-acetyl-2′-deoxyuridine (3.00 g, 9.6 mmol) was treated with trifluoroacetic acid (3.43 g, 29 mmol) and xenon difluoride (3.25 g, 19 mmol) to give 11 (1.21 g, 33% yield) after purification with silica gel chromatography ($CHCl_3$/EtOH, 20:1): amorphous powder; MS [field desorption (FD) method], $m/e$ 380 ($M^+$); $^1H$ NMR $\delta$ 2.05 (s, 3 H), 2.10 (s, 3 H), 2.30–2.60 (m, 2 H), 4.20–4.50 (m, 4 H), 5.10–5.35 (m, 1 H), 6.10–6.40 (dd, 1 H, $J$ = 8 Hz), 8.00 (1 H, s), 9.30 (br s, 1 H); $^{19}F$ NMR $\phi$ 67.0 (s, 3 F).

**3′,5′-Di-*O*-acetyl-5-(pentafluoroethyl)-2′-deoxyuridine (12):** yield 31%; mp 117–119 °C; MS (FD method), $m/e$ 430 ($M^+$); $^1H$ NMR $\delta$ 2.05 (s, 3 H), 2.10 (s, 3 H), 2.30–2.60 (m, 2 H), 4.20–4.50 (m, 4 H), 5.10–5.35 (m, 1 H), 6.10–6.40 (dd, 1 H, $J$ = 8 Hz), 8.00 (1 H, s), 9.30 (br s, 1 H); $^{19}F$ NMR $\phi$ 112.5 (s, 2 F), 84.0 (s, 3 F). Anal. Calcd for $C_{15}H_{15}F_5N_2O_7$: C, 41.87; H, 3.51; N, 6.51. Found: C, 42.01; H, 3.52; N, 6.50.

**5-(Trifluoromethyl)-2′-deoxyuridine (13).** The diacetoxy compound 11 (0.380 g, 1 mmol) was treated with a saturated ammonia solution of methanol (2 mL) at room temperature for 10 h and evaporated in vacuo to give the residue. To the crude products was added hexane/ether (1:1) at 0 °C to give the crystals (0.243 g, 82% yield): mp 179–182 °C (lit.[9b] mp 182–183 °C); MS (FD method), $m/e$ 296.

**5-(Pentafluoroethyl)-2′-deoxyuridine (14):** mp 172–175 °C; MS (FD method), $m/e$ 346; $^1H$ NMR ($CD_3OD$) $\delta$ 2.30–2.40 (m, 2 H), 2.80 (br s, 2 H), 3.80 (d, 2 H, $J$ = 8 Hz), 3.90–4.00 (m, 1 H), 4.15 (br s, 1 H), 4.40–4.50 (m, 2 H), 6.10–6.30 (m, 1 H), 8.70 (br s, 1 H); $^{19}F$ NMR ($CD_3OD$) $\phi$ 112.5 (s, 2 F), 84.0 (s, 3 F). Anal. Calcd for $C_{11}H_{11}F_5N_2O_5$: C, 38.16; H, 3.20; N, 8.09. Found: C, 38.10; H, 3.11; N, 8.01.

***N*-[2-(Trifluoromethyl)-4-(trimethylsilyl)phenyl]acetamide (15) and *N*-[3-(Trifluoromethyl)-4-(trimethylsilyl)phenyl]acetamide (16).** *N*-[4-(Trimethylsilyl)phenyl]acetamide (207 mg, 1 mmol) was treated with xenon difluoride (254 mg, 1.5 mmol) and trimethylsilyl trifluoroacetate (372 mg, 2 mmol) to give **15** (92 mg, 34%) and **16** (23 mg, 8%) after silica gel chromatography ($CHCl_3$/AcOEt, 20:1). Compound **15**: mp 133.5–134.5 °C; MS, $m/e$ 275 ($M^+$); $^1H$ NMR $\delta$ 0.30 (s, 9 H), 7.30–7.60 (br s, 1 H), 7.60–7.80 (m, 2 H), 8.00–8.30 (m, 1 H); $^{19}F$ NMR $\phi$ 63.5 (s, 3 F). Anal. Calcd for $C_{12}H_{16}F_3NOSi$: C, 52.34; H, 5.86; N, 5.09. Found: C, 52.21; H, 5.58; N, 4.99. Compound **16**: mp 78–80 °C; MS, $m/e$ 275 ($M^+$); $^1H$ NMR $\delta$ 0.30 (s, 9H), 7.42–7.90 (m, 3 H), 8.10–8.30 (br s, 2 H); $^{19}F$ NMR $\phi$ 60.5 (s, 3 F).

**2-Chloro-5-(trimethylsilyl)benzotrifluoride (17) and 2-(Trimethylsilyl)-5-chlorobenzotrifluoride (18). Method A.** After the reaction, the mixture was treated with a 10-fold excess of trifluoroacetic acid at room temperature to convert (4-chlorophenyl)trimethylsilane left to chlorobenzene (protodesilylation). By the procedure, trifluoromethylated compounds could be easily separated from the mixtures: bp 150 °C (oven temp) (14 mmHg); net yields are 30% (17) and 8% (18) checked by GLC analysis (OV-17, 2.0 × 3 mm, column temp 80 °C. Compound **17**: $^1H$ NMR $\delta$ 0.18 (s, 9 H), 7.30–7.70 (m, 3 H); $^{19}F$ NMR $\phi$ 62.0 (s, 3 F); HRMS calcd for $C_{10}H_{12}ClF_3Si$ 252.0350, found 252.0341. Compound **18**: $^1H$ NMR $\delta$ 0.18 (s, 9 H), 7.30–7.70 (m, 3 H); $^{19}F$ NMR $\phi$ 58.5 (s, 3 F); HRMS found 252.0333.

**Acknowledgment.** We thank Professor Andrew S. Kende of the University of Rochester for fruitful discussions.

**Registry No.** **1**, 98-08-8; **2A**, 320-50-3; **2B**, 115591-62-3; **2C**, 115591-63-4; **3a**, 115591-64-5; **3b**, 115591-65-6; **4a**, 115591-66-7; **4b**, 115591-67-8; **5a**, 348-90-3; **5b**, 344-53-6; **6a**, 114973-35-2; **6b**, 1994-23-6; **6c**, 115591-68-9; **7a**, 115603-77-5; **7b**, 115591-69-0; **8a**, 115591-71-4; **8b**, 115591-72-5; **9a**, 38609-76-6; **9b**, 115591-73-6; **10**, 104939-25-5; **11**, 65499-42-5; **12**, 84500-35-6; **13**, 70-00-8; **14**, 84500-36-7; **15**, 115591-74-7; **16**, 115591-75-8; **17**, 453-54-3; **18**, 115603-78-6; $XeF_2$, 13709-36-9; $CF_3CO_2H$, 76-05-1; $C_2F_5CO_2H$, 422-64-0; $C_3F_7CO_2H$, 375-22-4; benzene, 71-43-2; 1,4-dichlorobenzene, 106-46-7; methyl 4-chlorobenzoate, 1126-46-1; 3,4-dimethoxy-1-nitrobenzene, 709-09-1; *N*-[4-chlorophenyl]acetamide, 539-03-7; *N*-[2,5-difluorophenyl]acetamide, 398-90-3; *N*-[3,5-dichlorophenyl]acetamide, 31592-84-4; isopropyl 5-acetamido-4-fluorobenzoate, 115591-70-3; 1,2-dihydro-2-oxo-5-(trifluoromethyl)pyridine, 33252-63-0; methyl 2-furancarboxylate, 611-13-2; 3′,5′-di-*O*-acetyl-2′-deoxyuridine, 13030-62-1; *N*-[4-(trimethylsilyl)phenyl]acetamide, 17983-71-0; trimethylsilyl trifluoroacetate, 400-53-3; (4-chlorophenyl)trimethylsilane, 10557-71-8.

## Facile Isomerization of 2-(Dicyanomethylene)-1,3-indandione to 2,3-Dicyano-1,4-naphthoquinone

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There is considerable interest in highly conjugated, planar, electron-acceptor molecules that form stable anion radical salts with appropriate cationic species, as many of these salts are organic semiconductors or organic metals.[1]

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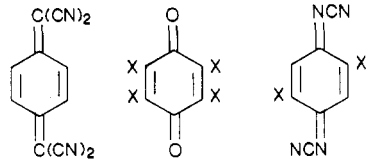
In this context the archetypal acceptor is 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ) (1), and a galaxy of complexes of TCNQ with metal cations, ammonium, phosphonium, and related cationic species have been characterized in the solid state.[1,2] Other related acceptors that form crystalline conducting salts are *p*-halobenzoquinones (2)[3] and N,N'-dicyanoquinonediimines (3).[4]



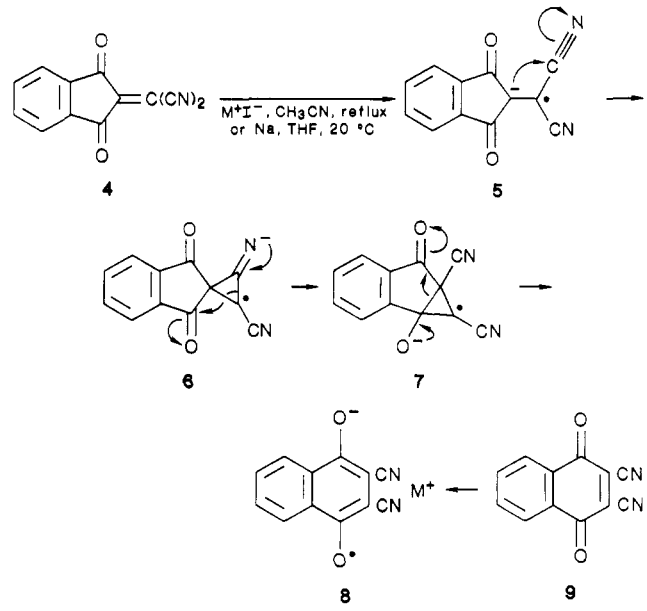
1 2, X = Cl, Br 3, X = H, Me, Cl

As part of a program of work directed toward the study of acceptors with different symmetry and/or skeletal structures from 1–3 that may be expected to form stable, delocalized radical anions, we turned our attention to molecule 4, prepared from indan-1,3-dione and tetracyanoethylene.[5] Reduction of 4 with cationic iodides, which we anticipated would lead to stable salts of 4, by analogy with TCNQ (1),[6] instead initiated a fascinating rearrangement to afford crystalline salts of the isomeric 2,3-dicyano-1,4-naphthoquinone (9). Salts **8a** and **8b** have been obtained by this method in 94% and 45% yields, respectively.

The lithium salt **8a** was identified by IR comparisons with an authentic sample prepared from lithium iodide and 2,3-dicyano-1,4-naphthoquinone (9),[7] and the structure of the product (**8b**) formed from reaction of 4 with methyltriphenylphosphonium iodide was confirmed by X-ray analysis.[8] Furthermore, treatment of salts **8a** and **8b**, prepared from 4, with concentrated hydrochloric acid, as described previously for authentic **8a**,[7] led to isolation of 2,3-dicyano-1,4-naphthoquinone (9) in 65% and 40% yields, respectively. Under these acidic conditions, compound 4 was recovered unchanged in quantitative yield.

The notable features of the isomerization of 4 into 9 are the ring expansion of the indandione skeleton into the naphthoquinone skeleton with the formal 1,2-migration of a cyanide group. This rearrangement could be promoted either by nucleophilic addition of iodide ion to the highly electrophilic carbon of the dicyanomethylene group of 4 or by one-electron transfer from the iodide ion. Evidence for the latter mechanism has been obtained, by observing that treatment of compound 4 with sodium metal suspended in tetrahydrofuran also brings about isomerization. From this reaction sodium salt **8c** was isolated in 22% yield, identical by IR spectra with an authentic sample obtained from sodium iodide and quinol salt **8a**. The mechanism we favor for the isomerization is shown in Scheme I. One-electron transfer to compound 4 yields the symmetrical radical anion **5**, which can ring close to give spirocyclopropane intermediate **6**. Rearrangement of

**Scheme I**[a]



[a] (a) M = Li, (b) M = $Ph_3PMe$, (c) M = Na.

6 via a ring opening–ring closure sequence yields a second cyclopropane intermediate 7 in which one cyanide group has formally migrated. Ring opening of intermediate 7 affords the naphthoquinol system and the salts 8, which are isolated.

## Experimental Section

**Preparation of Salt (8a).** To a boiling solution of 2-(dicyanomethylene)-1,3-indandione (4) (1.0 g, 4.8 mmol) dissolved in dry acetonitrile was added lithium iodide (0.96 g, 7.2 mmol) in one batch. The solution, which instantly turned dark, was heated at reflux for 1 h, cooled to room temperature, and filtered to yield the lithium salt of 2,3-dicyano-1,4-naphthoquinone as a dark green powder (0.97 g, 94%): IR (Nujol) 2235, 1562, 1501, 1271, 1170, 1144, 890, 780, and 691 $cm^{-1}$. Anal. Calcd for $C_{12}H_4N_2LiO_2$: C, 67.0; H, 1.9; N, 13.0. Found: C, 66.9; H, 1.9; N, 13.1.

This material was identical (by IR comparison) with the salt prepared in 45% yield from reaction of lithium iodide with authentic 2,3-dicyano-1,4-naphthoquinone (prepared from 2,3-dichloro-1,4-naphthoquinone and sodium cyanide) as described previously.[7]

**Preparation of Salt 8b. Via** the same procedures described above, reaction of methyltriphenylphosphonium iodide and compound 4 in acetonitrile afforded salt **8b** in 45% yield as a black crystalline solid: IR (Nujol) 2195, 1542, 1501, 1268, 1112, 915, 907, 751, 740, 718, 691, 505, and 498 $cm^{-1}$. Anal. Calcd for $C_{31}H_{22}N_2O_2P$: C, 76.7; H, 4.6; N, 5.8. Found: C, 76.2; H, 5.0; N, 5.4. Salt **8b** was also prepared in 93% yield from reaction of salt **8a** and methyltriphenylphosphonium iodide in water.

Treatment of salts **8a** and **8b** with concentrated hydrochloric acid, followed by workup as described previously,[7] yielded naphthoquinone 9 in 65% and 40% yields, respectively. Compound 9 prepared by this route was identical (melting point and IR comparison) with the authentic sample, prepared by the literature route[7] (our samples had mp 260 °C; lit.[7] mp 274–275 °C).

**Preparation of Salt 8c.** Compound 4 (300 mg, 1.5 mmol) was dissolved in dry tetrahydrofuran (5 mL), and finely cut sodium metal (33 mg, 1 mol equiv) was added. The mixture was stirred at room temperature for 48 h. The precipitate was filtered, washed with ether, and dried to afford salt **8c** as a green solid (75 mg, 22%): IR (Nujol) 2210, 1565, 1545, 1492, 1442, 1270, 1170, 1145, 890, and 700 $cm^{-1}$. Compound **8c** prepared by this route was identical (IR comparison) with a sample prepared from lithium salt **8a** and sodium iodide in water.

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**Registry No.** 4, 16954-74-8; 8a, 95028-79-8; 8b, 57133-84-3; 8c, 35670-43-0; 9, 1018-78-6.

## 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in Aqueous Acetic Acid, a Convenient New Reagent for the Synthesis of Aryl Ketones and Aldehydes via Benzylic Oxidation

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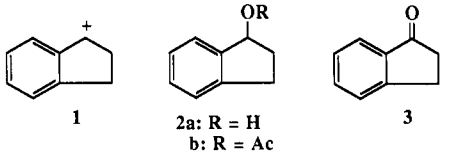
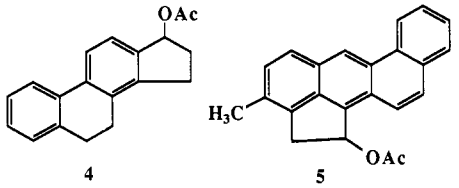
2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in aqueous media was shown in a prior study to be a useful reagent for the oxidation of arylalkanes to yield aryl ketones and aldehydes.[1] In subsequent investigations we have found that DDQ in aqueous acetic acid is potentially of broader synthetic utility, exhibiting greater regioselectivity and affording higher yields of desired products. In Table I are summarized the results of oxidation of a large series of arylalkanes with this reagent.

The mechanism of these oxidations is thought to involve initial hydride abstraction by DDQ at a benzylic site to form a stabilized carbocation (1), which is trapped by relatively rapid reaction with acetic acid to form the acetate ester (**2b**) of the corresponding benzylic alcohol. Further oxidation of this intermediate may proceed via a second hydride abstraction at the same benzylic site or acid-catalyzed hydrolysis to yield the free alcohol **2a**, which is further oxidized to the carbonyl compound **3** by DDQ.[2,3] Under appropriate conditions the benzylic acetoxy intermediate may be isolated. Thus, when 6,7,16,17-tetrahydro-15*H*-cyclopenta[*a*]phenanthrene was treated with 1 equiv of DDQ in nonaqueous HOAc or when 3-methylcholanthrene was reacted with DDQ in aqueous HOAc at room temperature, the corresponding acetoxy compounds, **4** and **5**, were isolated as the principal products.




1 2a: R = H b: R = Ac 3

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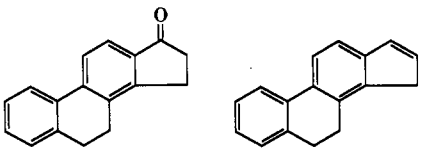
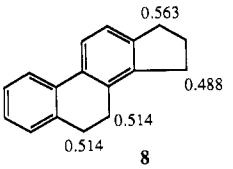
The success of this method is dependent upon the efficacy of trapping of the carbocation intermediates, the rate of which must exceed the loss of a proton to form a dehydrogenated product. Dehydrogenation is, of course, a well-known pathway for quinone oxidations.[2,4] Acetic acid appears considerably more effective than water as a trapping agent. Thus, oxidation of 6,7,16,17-tetrahydro-15*H*-cyclopenta[*a*]phenanthrene with DDQ in aqueous $CHCl_3$ provided a mixture of the ketone 6,7,16,17-tetrahydro-15*H*-cyclopenta[*a*]phenanthren-17-one (**6**) and the olefin 15*H*-cyclopenta[*a*]phenanthrene (**7**) in approximately equal ratio. In contrast, analogous reaction with DDQ in aqueous acetic acid furnished **6** as the sole identifiable product in 76% yield.




6 7

The DDQ/HOAc/$H_2O$ reagent exhibits remarkable regioselectivity. In cases where multiple benzylic sites are present in the molecule, as in 6,7,16,17-tetrahydro-15*H*-cyclopenta[*a*]phenanthrene (**8**) the precursor of **6**, oxidative attack tends to occur selectively at a single site. Moreover, there appears to be minimal propensity for oxidation beyond the monocarbonyl stage. The site of initial hydride abstraction is that which affords the most stable carbocation intermediate predictable theoretically from the calculated $\beta$-delocalization energies.[1,5,6] Thus, in the case of **8**, the calculated values of $\Delta E_{deloc}$ for the benzylic carbocations at the C-6, -7, -15, and -17 positions are 0.514, 0.514, 0.488, and 0.563 $\beta$, respectively, and the principal product of reaction is **6** arising from oxidation at C-17.[7] Similarly, oxidation of 7,8,9,10-tetrahydrobenzo[*a*]pyrene (**9**) occurs exclusively at position C-10, which has the highest value of $\Delta E_{deloc}$ (0.794 $\beta$).

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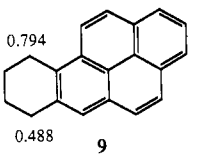


9

Methoxy and alkyl substituents at sites conjugated with the incipient carbocation intermediate markedly enhance

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