electrophilicity approximately that of an acid chloride or very reactive anhydride or isocyanate are required. Further, it has been shown that the bicyclic ring system is stable to nucleophilic and oxidative reaction conditions, as well as strong acid such as PPA. These results should lead to interesting and useful future chemistry.

Experimental Section

Melting points were determined in open capillaries and are uncorrected. NMR spectra were measured at 60 MHz. Mass spectra were determined with a Varian MAT CH_4 spectrometer. Percolations were done with Merck silica gel 60. Microanalysis were performed by the analytical department of Syntex Research.

General Procedure. To a solution of 1 was added an excess of electrophilic reagent (reaction solvent and times as noted in Table I). Reactions were run at room temperature except as noted in Table I. Either workup A or B, which are described below, was utilized.

Workup A. The reaction mixture was evaporated to a solid and dissolved in methylene chloride. The solution was passed through a pad of silica gel and eluted with a 0–5% methanol/methylene chloride gradient. The eluent was then evaporated to a solid.

Workup B. The reaction mixture was poured into water, extracted with methylene chloride, dried over anhydrous sodium sulfate, and evaporated to a solid. The residue was passed through a pad of silica gel as above.

Anhydro-2-acetyl-2-hydroxythiazolo[3,2-*a*]pyridinium Hydroxide (7). To a solution of 1.0 g (5.9 mmol) of 1 in 25 mL of THF was added 4.2 mL (59 mmol) of acetyl chloride. The reaction mixture was stirred for 18 h at room temperature. Workup A was used and the product crystallized from EtOAc to give 0.8 g (70%) of 7.

Anhydro-2-[2-(phenylthio)acetyl]-3-hydroxythiazolo[3,2-*a*]pyridinium Hydroxide (9). To a solution of 500 mg (2.2 mmol) of 8 in 15 mL of DMF were added 0.3 mL (2.5 mmol) of thiophenol and 75 mg (3.1 mmol) of sodium hydride. After the mixture was stirred for 18 h at room temperature, workup B was used. The product was crystallized from CH_2Cl_2/hexane to give 300 mg (46%) of 9.

Anhydro-2-[2-(phenylsulfinyl)acetyl]-3-hydroxythiazolo[3,2-*a*]pyridinium Hydroxide (10). A solution of 600 mg (2 mmol) of 9 in 25 mL of methylene chloride was cooled to −5 °C in an ice/acetone bath and 0.42 mL (2.5 mmol) of peracetic acid was added dropwise. After addition was complete, the reaction was stirred for 20 min. A solution of 475 mg (2.5 mmol) of sodium bisulfite in 25 mL of water was added dropwise, keeping the reaction temperature less than 0 °C. The reaction solution was then neutralized with aqueous sodium bicarbonate and workup B employed. The product was crystallized from CH_2Cl_2/hexane to give 300 mg (48%) of 10.

Registry No. 1, 10002-29-6; 6, 80484-74-8; 7, 73195-67-2; 8, 80484-75-9; 9, 80484-76-0; 10, 80484-77-1; 11, 80484-78-2; 12, 80484-79-3; 13, 80484-80-6; 14, 80484-81-7; 15, 80484-82-8; 16, 80484-83-9; 17, 80484-84-0; 18, 80484-85-1.

Role of Sodium Benzoate in the Reaction of 7,7,8,8-Tetracyanoquinodimethane with Acetone: Use of Salicylate as a Test for Carboxyl Radical

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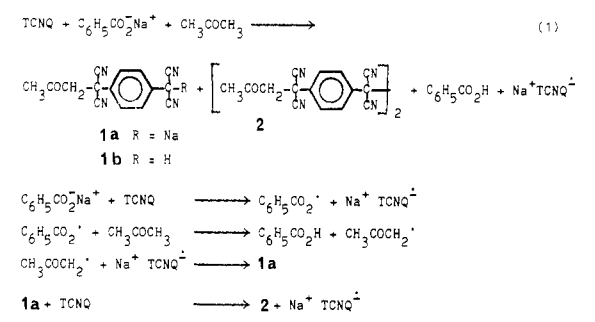
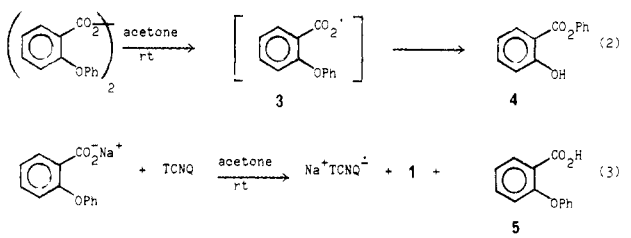
In 1976 Russell and Farcasiu reported a reaction between 7,7,8,8-tetracyanoquinodimethane (TCNQ) and acetone, in the presence of sodium benzoate, producing adduct **1a** and its dimer **2**.[1] The mechanism these authors proposed for the transformation (Scheme I) involves oxidation of sodium benzoate by TCNQ to give the benzoyloxy radical and the TCNQ radical anion. This oxidation seemed to be general, because other carboxylates similarly "reduced" TCNQ. It is curious, however, that no decarboxylation was observed for any of the carboxylates tested.[2] The novelty of this carboxylate oxidation by an organic reagent, as well as our continuing interest in TCNQ chemistry,[3] prompted us to further investigate the mechanism of this reaction. We now report the results of that work.

Scheme I



Scheme II



In our repetition of the sodium benzoate reaction (eq 1) we found all of the reaction products previously reported;[1] in addition, we isolated adduct **1b**, the protonated form of **1a** that had been characterized earlier. The new material **1b** was partially deprotonated by sodium benzoate in acetone to give **1a**. Furthermore, compound **1b** was identical (IR, NMR) with a sample independently synthesized by alkylating *p*-phenylenedimalononitrile with bromoacetone; this synthesis constitutes a structural proof for **1a**.

In an attempt to demonstrate the intermediacy of the benzoyloxy radical in eq 1, the sequence of experiments outlined in Scheme II was performed. The decomposition of 2-phenoxybenzoyl peroxide in refluxing benzene has been investigated[4] and was shown to yield phenyl salicylate (**4**) as the main product. It was further demonstrated that this reaction proceeds via the corresponding benzoyloxy radical (**3**), which undergoes phenyl migration, giving **4**. We ran the peroxide decomposition reaction in acetone at 25 °C—the conditions of the sodium benzoate/TCNQ reaction—and found that **4** is produced in the same yield as earlier reported.[5] Clearly, if the sodium benzoate re-

(1) M. Farcasiu and C. S. Russell, *J. Org. Chem.*, **41**, 571 (1976).

(2) Although phenyl carboxylate would not necessarily be expected to decarboxylate under the reaction conditions (as the authors in ref 1 point out), we also saw no decarboxylation for such substrates as triphenylacetate or sodium pivalate—compounds whose corresponding radicals should in principle decarboxylate much faster than the benzoyloxy case. C. S. Russell has described similar experimental results (private communication).

(3) (a) U.S. Patent 4 229 364, 1980; *Chem. Abstr.*, **94**, 120976k (1981); (b) U.S. Patent 4 148 811, 1979; *Chem. Abstr.*, **91**, 199076 (1979).

(4) D. F. DeTar and A. Hlynsky, *J. Am. Chem. Soc.*, **77**, 4411 (1955).

(5) The reaction is much slower at room temperature than in refluxing benzene (ref 4). The yield is the same, correcting for recovered starting material.

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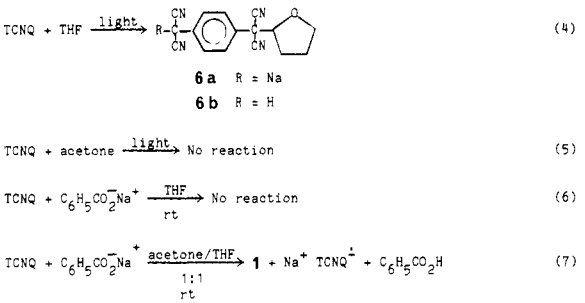
Scheme III



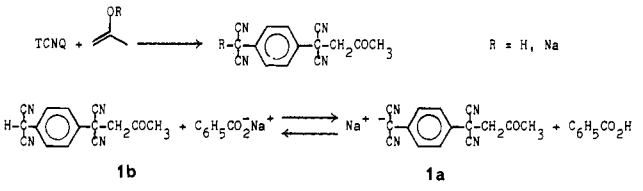
action (eq 1) involved direct oxidation of the carboxylate, then substitution of sodium 2-phenoxybenzoate for sodium benzoate should produce radical intermediate **3**; production of phenyl salicylate should then ensue, under the assumption that intramolecular migration would compete favorably with intermolecular abstraction of a hydrogen atom from acetone (as in Scheme I). The reaction was run (eq 3) and shown to produce TCNQ radical anion, **1**, and **5**; however, no trace of phenyl salicylate could be found in the product mixture. In a separate, control experiment, the reaction was repeated under identical conditions except that authentic phenyl salicylate was added, the amount corresponding to the expected yield based on eq 2. In addition to the products previously found, phenyl salicylate was easily detected in the product mixture. Considering these data, it is unlikely that the benzoyloxy radical is an intermediate in the reaction of TCNQ with sodium benzoate.

Further doubt is cast upon the mechanism in Scheme I by the experiments described in Scheme III. The reaction between TCNQ and THF to give adduct **6b** has been shown to occur both with a radical initiator and with initiation by a sunlamp.[6] We repeated this reaction to obtain an authentic sample of **6b** (which, upon deprotonation, gives anion **6a**). We attempted this reaction using acetone as solvent, but recovered only unreacted TCNQ. When THF replaced acetone as solvent for the sodium benzoate reaction (eq 6), only starting materials were recovered (this result, however, could be due to the exceedingly low solubility of sodium benzoate in THF). Most significantly, when a 1:1 mixture of acetone and THF was used (eq 7), all of the "normal" products were formed, but neither **6a** nor **6b** was present in the product mixture. If the mechanism of this reaction involved acetonyl and benzoyloxy radicals as intermediates, one would certainly have expected THF to compete with acetone as a hydrogen atom donor, leading to compounds **6a** and **6b**.

An alternative, hypothetical mechanism consistent with these experimental results is offered in Scheme IV. The key difference from the Scheme I mechanism is that the TCNQ/acetone adduct is produced by addition of the acetone enol or enolate to TCNQ by a polar mechanism. The addition of nucleophiles to TCNQ in this manner is documented.[7] The role of the sodium benzoate in the Scheme IV mechanism is simply to act as a base; anion **1a** may then be oxidized by TCNQ (as in Scheme I) to give the other observed products. Consistent with this mechanism is the fact that a low yield of compound **1b** is produced in a reaction between TCNQ, acetone, and tetrabutylammonium fluoride, a reaction that almost certainly involves a polar addition mechanism.[8]

(6) J. Diekmann and C. J. Pedersen, *J. Org. Chem.*, **28**, 2879 (1963).
(7) (a) D. S. Acker and W. R. Hertler, *J. Am. Chem. Soc.*, **84**, 3370 (1962); (b) W. R. Hertler, H. D. Hartzler, D. S. Acker, and R. E. Benson, *J. Am. Chem. Soc.*, **84**, 3387 (1962).

Scheme IV



(Mechanism continues as in Scheme I)

Experimental Section

Melting points are uncorrected. NMR spectra were determined on a Varian EM-360A spectrometer and are expressed as δ values, parts per million downfield from Me_4Si as an internal standard. IR spectra were recorded on a Perkin-Elmer 298 spectrometer; mass spectra were recorded on an HP 5985B spectrometer.

TCNQ/Acetone Adduct 1b. A. Isolation from the Sodium Benzoate Reaction. A mixture of sodium benzoate (4.32 g), TCNQ (6.12 g), and 750 mL of acetone (dried over $CaCl_2$) was stirred for 2 days at room temperature as described in ref 1. The crude reaction mixture was filtered and concentrated in vacuo to dryness. After being washed with ether, the resulting black powder was extracted with hot methylene chloride to give crude **1b**. The NMR of this extract clearly indicated the presence of **1b**. The sample was purified by flash column chromatography (94:3:3 chloroform/methanol/glacial acetic acid) to give pure **1b** (R_f 0.33, same solvent) which could be recrystallized from methylene chloride/hexanes to give material with mp 143–5 °C. Although only 256 mg of **1b** was thus isolated, more could be seen in the NMR spectrum of the extraction residue. **1b**: ^1H NMR (acetone-d_6) δ 2.2 (s, 3 H), 3.85 (s, 2 H), 7.8 (s, 4 H); IR (KBr disk) 2250 (w), 1720 (s), 1620, 1505, 1410, 1395, 1350, 1160, 850 cm^{-1}; exact mass [NH_3 CI; m/z 280 $(M + NH_4)^+$] calcd 280.1197, found 280.1208.

B. Independent Synthesis. To a solution of 860 mg of *p*-phenylenedimalononitrile[7a] in 125 mL of freshly distilled THF, stirred under argon, was added 4.1 mL of 1 N sodium hydroxide. After 5 min, 3.8 mL of bromoacetone (excess) was added, and the reaction mixture was stirred at 25 °C for 12 h. Glacial acetic acid (3 mL) was added, and the reaction mixture was concentrated in vacuo to dryness. The residue was washed well with ether and then taken up in a small volume of acetone and filtered. The filtrate was concentrated and again taken up in acetone and filtered (to remove the last of the NaBr). Upon concentration and drying, 580 mg of yellow solid was obtained. This material was fairly pure (IR) but could be further purified as in method A.

C. Tetrabutylammonium Fluoride (TBAF) Method. To a solution of 300 mg of TCNQ in 35 mL of dry acetone was added 1.47 mL of 1 N TBAF (solution in THF) via syringe. After the mixture was stirred for 12 h at 25 °C, it was filtered and concentrated in vacuo. The crude reaction was purified as in method A, except that two successive flash columns were necessary. The yield of **1b** was 21 mg (5%). Also present in the product mixture was *p*-phenylenedimalononitrile (R_f 0.4, 94:3:3 chloroform/methanol/glacial acetic acid).

Reaction of Sodium 2-Phenoxybenzoate with TCNQ in Acetone. A slurry of 0.86 g of TCNQ (4.23 mmol) and 1.0 g of sodium 2-phenoxybenzoate (4.23 mmol) in 150 mL of acetone was protected from light and stirred at 25 °C for 136 h. The reaction mixture was filtered and the resulting solid was washed with water and air-dried to give 200 mg of TCNQ radical anion sodium salt. The original (acetone) filtrate was concentrated to dryness, giving a solid which was successively extracted with ether, hot methylene chloride, and hot ethyl acetate. All three extracts were separately concentrated to ca. 1 mL. Each was heavily spotted on a TLC plate alongside an authentic reference sample of phenyl salicylate (R_f 0.56, using 5:1 hexane/ethyl acetate). No trace of phenyl salicylate could be seen in the three concentrated extracts. Flash chromatography on the three combined extracts (following pro-

(8) J. H. Clark, *Chem. Rev.*, **80**, 429 (1980).

cedure A above) yielded pure **1b** (250 mg) along with ca. 400 mg of 2-phenoxybenzoic acid.

In a separate, control experiment, 0.76 g of TCNQ (3.72 mmol), 0.88 g of sodium 2-phenoxybenzoate (1 equiv), 0.20 g of authentic phenyl salicylate (0.25 equiv), and 200 mL of acetone were mixed as above and stirred at 25 °C for 137 h. During that time, aliquots from the reaction were periodically removed, concentrated, and spotted on TLC (5:1 hexane/ethyl acetate). Phenyl salicylate was easily detected throughout the course of the reaction as a strongly UV-active spot, R_f 0.56, alongside an authentic sample. At the end of the reaction, pure phenyl salicylate was isolated from the crude reaction mixture by flash chromatography followed by preparative TLC (26.5 mg, 13% recovery).

Acetone/THF Mixture as Solvent for the Sodium Benzoate Reaction. To a slurry of TCNQ (2.04 g, 10 mmol) and sodium benzoate (1.44 g, 10 mmol) in 125 mL of acetone (dried over calcium chloride) was added 125 mL of THF (freshly distilled). This mixture was protected from light and stirred at 25 °C for 67 h. The mixture was then filtered and concentrated in vacuo. The resulting solid was extracted with hot methylene chloride. After concentration, that extract was inspected by TLC (94:3:3 chloroform/methanol/acetic acid). A spot corresponding to **1b** was clearly present. No spot corresponding to **6b** could be seen (authenic **6b** obtained exactly according to ref 6 was spotted alongside the extract for reference). Compound **1b** was then isolated from the extract by flash chromatography as described in method A above to give 190 mg of **1b**.

The methylene chloride insoluble part of the reaction mixture was extracted with hot ethyl acetate to give, after concentration, a black powder. No **6a** could be seen in the NMR and IR spectra of that powder (authentic **6a** was obtained by deprotonation of **6b** with sodium hydroxide).

Acknowledgment. We are grateful to Dr. Charlotte S. Russell for providing an authentic sample of dimer **2**. We also thank Professor Ernest Wenkert for suggesting the tetrabutylammonium fluoride reaction. Helpful discussions with Dr. Robert J. Crawford are acknowledged.

Registry No. 1b, 80515-70-4; sodium benzoate, 532-32-1; 7,7,8,8-tetracyanoquinodimethane, 1518-16-7; acetone, 67-64-1; *p*-phenylenedimalononitrile, 18643-56-6; tetrabutylammonium fluoride, 429-41-4; sodium 2-phenoxybenzoate, 5138-68-1; phenyl salicylate, 118-55-8.

Stereospecific Syntheses of *endo*- and *exo*-1-Hydroxy-2,3,3a,4,5,6,7,7a-octahydro-*exo*-4,7-methano-1*H*-indene

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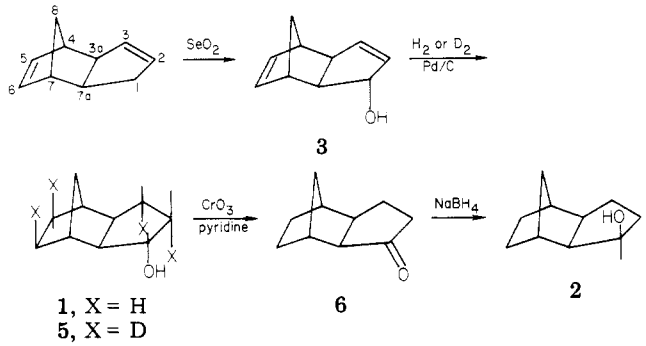
The dicyclopentadiene molecule and its hydrogenated derivatives are the basic structures for a variety of compounds from pesticides to jet fuels. The metabolism of these compounds tends to proceed via hydroxylation at the C_1 carbon. Although there have been numerous reports on the preparation of the hydroxylated derivatives of *endo*-dicyclopentadiene,[1] this paper reports the first preparation of the 1-hydroxy derivatives of the *exo*-dicyclopentadiene molecule.

exo-Dicyclopentadiene was treated with selenium dioxide (SeO_2) by using the allylic hydroxylation procedure of Woodward and Katz[2] to give *endo*-1-hydroxy-3a,4,7,7a-tetrahydro-*exo*-4,7-methano-1*H*-indene (**3**). The IR showed a broad band at 3200 cm^{-1}. The stereochemistry of **3** was established by noting that the carbinol proton in the ^1H NMR appeared as a doublet of doublets with J = 2 and 3 Hz. The small coupling constant indicated an anti arrangement for H_1 and H_{7a}[3]. A Dreiding model of **3** predicts a dihedral angle of approximately 120° if H_1 and H_{7a} are anti, which would lead to a coupling constant of 1-3 Hz[4]. Since H_{7a} is endo, H_1 must be exo, and the OH group must be endo. It is noteworthy that the major product of SeO_2 oxidation of *endo*-dicyclopentadiene is *exo*-1-hydroxy-3a,4,7,7a-tetrahydro-*endo*-4,7-methano-1*H*-indene (**4**).[2] In the cases of both *endo*- and *exo*-dicyclopentadiene the large SeO_2 molecule approaches the allylic group from the least hindered side to give exclusively the requisite alcohol.

Scheme I



Catalytic reduction of **3** over 5% palladium on charcoal yielded **1**. The ^1H NMR spectrum showed the absence of peaks in the 5.5-6.5-ppm range, indicating that the reduction of the olefinic groups was complete.

Catalytic reduction of **3** with deuterium on Pd/C yielded 1-*2,3,5,6-d*$_4$ (**5**). It was assumed that the deuterium added exo to the 5,6-positions.[5] Examination of ^1H NMR showed that proton H_1 was still a doublet of doublets but now with J = 2 and 9 Hz. This indicated that since H_1 and H_{7a} were anti, H_1 and H_2 were eclipsed. For H_1 and H_2 to be approximately eclipsed required that the deuteriums approached from the endo side.

By use of a modification of the Sarrett reaction,[6] **3** was oxidized to 2,3,3a,4,5,6,7,7a-octahydro-*exo*-4,7-methano-1-indenone (**6**). The IR showed a strong band at 1685 cm^{-1} (C=O) and absence of a band in the 3200-cm^{-1} (OH) region. The ^1H NMR showed only a multiplet at δ 0.95-2.55.

Sodium borohydride ($NaBH_4$) reduction of **6** gave **2**. The IR spectrum showed a strong band at 3250 cm^{-1}. The ^1H NMR showed peak at 3.70 ppm, which was assigned to the proton H_1. The large coupling constants of J = 8 and 10 Hz for the carbinol hydrogen indicated that the OH group must be exo so that H_1 is approximately eclipsed by H_2. A coupling between H_1 and H_2 anti is small (J = 1 Hz) and could be seen only by changing the NMR sweep width. There was no trace by GLC of any **1** being formed by the $NaBH_4$ reduction. Thus, BH_4^- like SeO_2 and H_2 all approach from the least sterically hindered side which

(1) H. C. Brown, I. Rothberg, and D. L. Vander Jagt, *J. Org. Chem.*, **37**, 4098 (1972).
(2) R. B. Woodward and T. J. Katz, *Tetrahedron*, **5**, 70 (1959).
(3) (a) W. T. Scroggins, M. F. Rettig, and R. M. Wing, *Inorg. Chem.*, *15*, 1381 (1976). (b) E. Kleinpeter, H. Kuhn, and M. Muhlstadt, *Org. Magn. Reson.*, **9**, 312 (1977).
(4) Karplus equation: V. M. Parikh, "Absorption Spectroscopy of Organic Molecules", Addison-Wesley, Menlo Park, CA, 1974, p 123.
(5) Deuterium has been shown to add exo to the 5,6-positions of *endo*-dicyclopentadiene.[3a] Addition to the norborene molecule always occurs from the exo side unless the exo side is blocked by substituents in the 7-position (J. March, "Advanced Organic Chemistry", 2nd ed., McGraw-Hill, New York, 1977, p 680).
(6) R. Ratcliffe and R. Rodehorst, *J. Org. Chem.*, **35** 4000 (1970).

0022-3263/82/1947-1140$01.25/0