hexane–benzene (9:1) the methyl enol ether of **9a**: 780 mg (40%); mp 146–148 °C (ether). Further elution gave **10a**: 848 mg (44%); mp 197–199 °C (acetone–hexane).

(3) 1-*tert*-Butylbenzo[*a*]pyrene (1a). A mixture of **10a** (434 mg, 1.5 mmol), anhydrous hydrazine (9.2 mmol), and 350 mg of KOH in 15 mL of diethylene glycol was heated at reflux for 4 h. The solvent was allowed to evaporate until the interior temperature rose to 236 °C, and then refluxing was continued for 4 h more. The usual workup and filtration through a short column of Florisil gave crude **1a** (440 mg, 100%) which was recrystallized twice from hexane to afford pure **1a**: 219 mg (50%); mp 179–181 °C; NMR, Table I.

Synthesis of 2-*tert*-Butylphenanthrene. (1) 2-(2-Phenanthryl)propanal (9b). Reaction of 2-acetylphenanthrene (8.81 g, 40 mmol) with dimethylsulfonium methylide by the method employed for the benzo[*a*]pyrene analogue yielded 2-(α-methyloxiranyl)phenanthrene (**8b**): 9.18 g (98%); mp 107–110 °C. Rearrangement of **8b** by the method described for **8a** gave **9b**: 6.96 g (74%); mp 53.5–56.5 °C (hexane); NMR ($CDCl_3$) δ 9.79 (s, 1, CHO), 7.56–8.75 (m, 9, aromatic), 3.82 (q, 1, CH), 1.57 (d, 3, CH_3). A second product was identified as the diol **11b**: 1.42 g; mp 166.5–167.5 °C; NMR ($CDCl_3$ + D_2O) δ 7.2–8.9 (m, 9, aromatic), 3.83 (br s, 2, CH_2), 1.67 (s, 3, CH_3).

(2) 2-Methyl-2-(-2-phenanthryl)propanal (10b). Treatment of **9b** (2.34 g, 10 mmol) with KH and MeI by the procedure described for **9a** furnished the corresponding dimethylated aldehyde **10b**: 1.76 g (71%); mp 100–101 °C (hexane); NMR ($CDCl_3$ δ 9.54 (s, 1, CHO), 7.52–8.64 (m, 9, aromatic), 1.56 (s, 6, CH_3). Detected as a minor product was the methyl enol ether of **9b**: 106 mg; mp 113–115 °C (hexane); NMR δ 7.46–8.67 (m, 9, aromatic), 6.61 (s, 1, vinylic), 3.75 (s, 3, CH_3O), 2.18 (s, 3, CH_3).

(3) 2-*tert*-Butylphenanthrene. Wolff–Kishner reduction of **10b** by the procedure for **10a** afforded 2-*tert*-butylphenanthrene: 245 mg (81%); mp 97–98 °C; a recrystallized sample melted at 98–98.5 °C (lit.[13] mp 99–100 °C); NMR δ 7.51–8.62 (m, 9, aromatic), 1.41 (s, 9, CH_3).

Synthesis of 1-*tert*-Butylpyrene. (1) 2-(1-Pyrenyl)propanal (9c). Reaction of 1-acetylpyrene (9.77) g, 40 mmol) with dimethylsulfonium methylide by the procedure employed in previous examples furnished 1-(α-methyloxiranyl)pyrene (**8c** 9.28 g) as a red oil. Rearrangement of **8c** as described for **8a** gave **9c**: 7.18 g (70%); mp 130–132 °C (ethanol); NMR δ 9.86 (s, 1, CHO), 7.73–8.19 (m, 9, aromatic), 4.63 (q, 1, CH), 1.69 (d, 3, CH_3).

(2) 2-Methyl-2-(1-pyrenyl)propanal (10c). Methylation of **9c** (2.58 g, 10 mmol) with KH and MeI by the method described for **9a** gave **10c**: 1.47 g (54%); mp 132–135 °C; the analytical sample melted at 135.5–137 °C (hexane); NMR δ 9.76 (s, 1, CHO), 7.73–8.24 (m, 9, aromatic), 1.70 (s, 6, CH_3). Also obtained as a minor product was the methyl enol ether of **9c**: 7.53 mg (28%); mp 79–81 °C (MeOH–H_2O); NMR δ 7.71–8.37 (m, 9, aromatic), 6.13 (s, 1, vinylic), 3.64 (s, 3, CH_3O), 2.22 (s, 3, CH_3).

(3) 1-*tert*-Butylpyrene (1a). Reduction of **10c** (681 mg) by the Wolff–Kishner method afforded 1-*tert*-butylpyrene: 487 mg (75%); mp 94–97 °C; recrystallization raised the melting point to 97.5–99 °C; NMR δ 7.89–8.77 (m, 9, aromatic), 1.72 (s, 9, CH_3).

Synthesis of 6-*tert*-Butylchrysene. (1) 1-(6-Chrysenyl)propanal (9d). Reaction of 6-acetylchrysene[14] with dimethylsulfonium methylide by the usual procedure furnished 6-(α-methyloxiranyl)pyrene (**8d**; 8.3 g, 97%) as a white solid. A solution of **8d** in minimal CH_2Cl_2 was adsorbed on 200 g of Florisil dried previously at 200 °C for 24 h. The column was allowed to stand for 1 h. Elution with benzene gave **9d**: 7.46 g (88%); mp 108–111 °C; the analytical sample melted at 112–114.5 °C (acetone–hexane); NMR δ 9.73 (s, 1, CHO), 7.42–8.67 (m, 11, aromatic), 4.28 (q, 1, CH), 1.56 (d, 3, CH_3).

(2) 2-Methyl-2-(6-chrysenyl)propanal (10d). Methylation of **9d** (4.27 g, 15 mmol) with KH and MeI by the usual method gave 4.29 g of crude product which was chromatographed on Florisil. Elution with hexane–benzene (9:1) afforded the methyl enol ether of **9d**: 2.41 g (54%); mp 171–173 °C; NMR δ 7.61–8.87 (m, 11, aromatic), 6.28 (s, 1, vinylic), 3.76 (s, 3, OCH_3), 2.2 (s, 3, CH_3). Elution with hexane–benzene (60–70%) gave **10d**: 1.55 g (35%); mp 131–134 °C; the analytical sample melted at 136–137 °C; NMR δ 9.87 (s, 1, CHO), 7.6–8.88 (m, 11, aromatic), 1.81 (s, 6, CH_3).

(3) 6-*tert*-Butylchrysene. Wolff–Kishner reduction of **10d** (448 mg) provided 6-*tert*-butylchrysene: 347 mg (81%); mp 107–109 °C; NMR δ 7.46–8.75 (m, 11, aromatic), 1.72 (s, 9, CH_3).

***tert*-Butylation of Pyrene.** A suspension of pyrene (4.04 g, 20 mmol) in 60 mL of trifluoroacetic acid and 4.8 mL (3.71 g, 50 mmol) of *tert*-butyl alcohol was heated at reflux with vigorous stirring for 2.5 h. The usual workup gave a semicrystalline residue which was dissolved in hot hexane and allowed to stand overnight. The precipitate of unreacted pyrene (2.33 g, mp 148–150.5 °C) was filtered off, and fractional crystallization of the residue from hexane gave 2,7-di-*tert*-butylpyrene: 540 mg; mp 206–208 °C (lit.[11] mp 208–209 °C); NMR δ 8.18 (s, 4), 8.02 (s, 4), 1.55 (s, 18, CH_3), in good agreement with the reported spectrum.[12]

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Registry No. 1a, 80484-51-1; **1b**, 4643-78-1; **2a**, 20916-70-5; **2b**, 80485-00-3; **3**, 518-85-4; **4**, 80484-52-2; **5**, 80484-53-3; **6**, 80484-54-4; **7**, 80484-55-5; **8a**, 80484-56-6; **8b**, 80484-57-7; **8c**, 80484-58-8; **8d**, 80484-59-9; **9a**, 80484-60-2; **9b**, 40452-15-1; **9c**, 80484-61-3; **9c** methyl enol ether, 80484-62-4; **9d**, 80484-63-5; **9d** methyl enol ether, 80484-64-6; **10a**, 80484-65-7; **10b**, 80484-66-8; **10c**, 80484-67-9; **10d**, 80484-68-0; **11a**, 80484-69-1; **11b**, 80484-70-4; benzo[*a*] pyrene, 50-32-8; 2,9-di-*tert*-butylbenzo[*a*]pyrene, 80484-71-5; 4-*tert*-butylbenzoyl chloride, 1710-98-1; 2-acetylphenanthrene, 5960-69-0; 2-*tert*-butylphenanthrene, 66553-04-6; 1-acetylpyrene, 3264-21-9; 1-*tert*-butylpyrene, 59527-71-8; 6-acetylchrysene, 33942-77-7; 6-*tert*-butylchrysene, 80484-72-6; pyrene, 129-00-0; 2,7-di-*tert*-butylpyrene, 24300-91-2.

(13) Fieser, L. F.; Price, C. C. *J. Am. Chem. Soc.* **1936**, *58*, 1838.
(14) Carruthers, W. *J. Chem. Soc.* **1953**, 3486.

A New Synthesis of Novel 2-Substituted Derivatives of the Anhydro-3-hydroxythiazolo[3,2-*a*]pyridinium Hydroxide Inner Salt Ring System[1]

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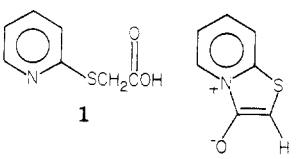
Initial reports[2] of the dehydration of (2-pyridylthio)-acetic acid (**1**) with acetic anhydride suggested **2** as the structure of the reaction product. Since then, other groups[3,4] have revised the structure and shown **3** to be the product. Probably **2** is indeed initially formed but is sufficiently nucleophilic at the 2-position that under the reaction conditions it reacts with a second molecule to form the dimeric compound **3**.



1

2

Authentic examples of the title ring system have been prepared by alkylation of 2-mercaptopyridine with sub-

(1) Contribution No. 608 from the Institute of Organic Chemistry, Syntex Research, Palo Alto, CA.
(2) G. F. Duffin and J. D. Kendal, *J. Chem. Soc.*, 734 (1951).
(3) K. T. Potts and D. R. Choudhury, *J. Org. Chem.*, *43*, 2700 (1978).
(4) L. T. Gorb et al., *Khim. Geterotsikl.* Soedin., 1066 (1979); *Chem. Abstr.*, *91*, 212554n (1979).

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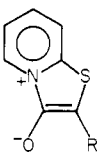
Table I[a]



compd	R	rctn time, h (solvent)	workup	mp, °C (solvent)	% yield
3	$O{=}CCH_2Spy$			183-185 (EtOH) (lit.[3] 187)	
4	Ph			lit.[5] 183-185	
5	$O{=}COCH_2CH_3$			166-167 (CH_2Cl_2/hexane) (lit.[6] 166.5-168)	
6	$O{=}CCF_3$	1 (trifluoroacetic anhydride)	A	195-198 (CH_2Cl_2/hexane)	45
7	$O{=}CCH_3$	18 (THF)	A	221-222 (EtOH)	70
8	$O{=}CCH_2Cl$	0.5 (toluene)[b]	B	210-214 (EtOH)	43
9	$O{=}CCH_2SPh$	18 (DMF)	B	133.5-139.5 (CH_2Cl_2/hexane)	46
10	$O{=}CCH_2S(O)Ph$	0.5 (CH_2Cl_2)	B	196-198 (CH_2Cl_2/hexane)	48
11	$O{=}CCH_2CO_2CH_2CH_3$	1 (DMF)	B	140-143 (CH_2Cl_2/hexane)	29
12	$O{=}CCH{=}CHPh$	1 (pyridine)	B	212-215 (CH_2Cl_2/hexane)	9
13	O=CH	1 (DMF)	B	233-234 (CH_2Cl_2/hexane)	57
14	CH=NNHPh	1 ($EtOH/H_2O$)[c]		166-168.5 (EtOH)	68
15	$O{=}CNH_2$	20 (polyphosphoric acid)	B	266-270 (CH_2Cl_2/hexane)	51
16	$O{=}CNHCO_2CH_3$	3 (pyridine)	B	239-243 (CH_2Cl_2/hexane)	16.8
17	O=CNHPh	2 (THF)		233-237 (CH_2Cl_2/hexane)	34
18	O=CPh	18 (THF)[c]	A	99.5-104.5 (CH_2Cl_2/hexane)	46
19	O=CCl				

[a] NMR and mass spectral data obtained were consistent with assigned structures. Satisfactory combustion analysis (±0.4%) for C, H, N, S, were obtained for all new compounds. [b] Heated at reflux. [c] Heated at 50 °C.

stituted α-haloacetic acid derivatives followed by cyclization. In this manner **4**[5] and **5**[6] have been prepared from bromophenylacetyl chloride and bromo(ethoxycarbonyl)-acetyl chloride, respectively. However, many potentially interesting α-haloacetic acids are not easily obtained and this procedure does not lend itself to the preparation of a wide variety of compounds.

In addition, there are reports[7,8] of the in situ generation of **2** from **1** with DCC followed by reaction with electrophiles such as diazonium salts and aromatic aldehydes.

Another approach to the preparation of 2-substituted derivatives of **2** appeared to be dehydration of **1** with a reagent sufficiently electrophilic that **2** initially formed would react with excess dehydrating agent rather than a second molecule of itself. Obviously, acetic anhydride is not reactive enough, but when **1** was treated with trifluoroacetic anhydride, **6** was easily isolated.[9] Acetyl chloride gave **7**,[10] and **8**, **11**, **12**, and **20** were obtained in an analogous manner from the corresponding acid chlorides. The chloroacetyl derivative **8** could be obtained by using either chloroacetyl chloride or chloroacetic anhydride. Reaction of **8** with thiophenol in DMF with sodium hydride gave **9** which was easily oxidized to **10** with peracetic acid. It is interesting to note that the ring system is stable to these conditions.

Compounds **11** and **12** were prepared in an attempt to produce tricyclic analogues by intramolecular cyclization with the oxygen at position 3. No cyclization was observed in either case.

The formyl derivative **13** could be prepared by reaction of **1** with acetic–formic anhydride or, more conveniently, with the Vilsmeier reagent derived from DMF–$POCl_3$. Hydrazone **14** was prepared by standard means. When **13** was subjected to Schmidt conditions[11] of sodium azide in polyphosphoric acid, the desired nitrile was not obtained but rather the amide **15**.

Reaction of **1** with phosgene gave a solution of an unstable material presumed to be **19**. Treatment of this solution with ethanol and with ammonium hydroxide gave **5** and **15**, respectively. Reaction with aniline afforded **17**. Attempts to hydrolyze **19** to the corresponding carboxylic acid failed to produce a recognizable product.

Reaction of **1** with alkyl and aryl isocyanates and isothiocyanates gave only **3** with the exception of carbomethoxy isocyanate which afforded **16**.

An interesting observation was made in repeating Potts' preparation of the dimeric compound, **3**.[3] In addition to **3**, a trace of another fluorescent compound was observed, which corresponded to the acetyl derivative (**7**). It was found that under Potts' reaction conditions, continued reflux led eventually to complete conversion of **3** to **7**. The same conversion could be obtained by refluxing preformed **3** with acetic anhydride. The corresponding benzoyl derivative (**18**) could be obtained in an analogous manner by refluxing **3** and benzoyl chloride in acetonitrile.

However, the use of **3** as a source of **2** did not succeed in any instance where using **1** failed, and appears to offer no synthetic advantage.

Small amounts of **3** are frequently found in reactions of **1** but are easily removed by chromatography. As these examples illustrate, a wide variety of derivatives of **1** may be easily prepared by this method. Reagents with an

(5) K. Undheim and P. O. Tveita, *Acta Chem. Scand.*, *25*, 5 (1971).
(6) K. T. Potts, S. J. Chen, J. M. Kane, and J. L. Marshall, *J. Org. Chem.*, *42*, 1633 (1977).
(7) L. T. Gorb et al., *Khim. Geterotsikl. Soedin.*, 1343 (1979); *Chem. Abstr.*, *92*, 128789f (1980).
(8) L. T. Gorb et al., *Dopos. Kad. Nauk. Urk. RSR, Ser. B.: Geol., Khim. Biol. Nauki*, 894 (1978); *Chem. Abstr.*, *90*, 38831t (1979).
(9) This reaction was first observed in these laboratories when (5-morpholinylcarbonyl)(2-pyridylthio)acetic acid was cyclized to the corresponding morpholino carbonyl analogue of **6**. T. Tompkins, C. C. Beard, J. O. Gardner, unpublished observation.
(10) H. Singh et al., *J. Chem. Res., Synop.*, 264 (1979).
(11) K. Masuda, J. Adachi, and K. Nomura, *J. Chem. Soc., Perkin Trans. 1*, 2349 (1979).

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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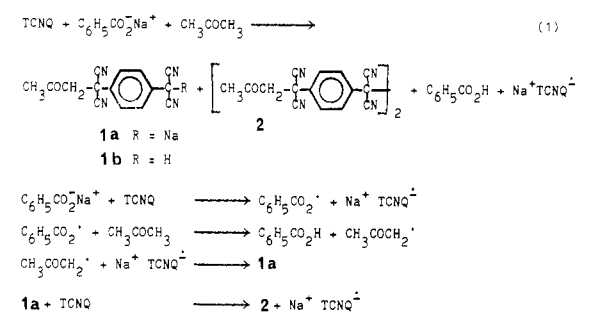
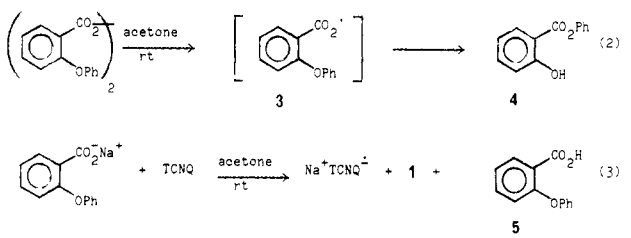
In 1976 Russell and Farcasiu reported a reaction between 7,7,8,8-tetracyanoquinodimethane (TCNQ) and acetone, in the presence of sodium benzoate, producing adduct **1a** and its dimer **2**.[1] The mechanism these authors proposed for the transformation (Scheme I) involves oxidation of sodium benzoate 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.

0022-3263/82/1947-1138$01.25/0