solution was cooled and treated dropwise with concentrated HCl (0.01 mol) and 30% H_2O_2 (0.01 mol) in that order. Dilution with Me_2CO resulted in the separation of a white solid, mp *ca.* 255°, that was identified as trimethylguanidine hydrochloride. Upon cooling the filtrate another crop of a white solid was obtained, mp 225°. This material was recrystallized from EtOAc-HOAc, mp 226-227° dec, then was converted to 18 with 70% $HClO_4$. The resulting perchlorate had mp 263-265° dec and was identical with the product from 9 and CH_3NH_2.

Conversion of 11 to 1,1-Dimethyl-3-[4-methyl-5-(methylimino)-1,2,4-dithiazolidin-3-ylidene]-2-thiourea (4). A mixture of 11 (0.286 g) and absolute EtOH (5 ml) was treated with 40% CH_3NH_2 (0.2 ml) at room temperature. After 2.5 hr crude 4 (0.131 g) was collected by filtration, mp 187-192°. Recrystallization from HOAc and then from 2-butanone gave material, mp 200-204°, whose ir and nmr spectra were identical with those of authentic 4.

Registry No.—**1b** HI, 51593-20-5; **3a**, 39656-37-6; **3b**, 39656-38-7; **4a**, 51593-03-4; **5**, 51592-79-1; **7a**, 51593-21-6; **7b**, 51593-22-7; **9a**, 51593-24-9; **11**, 51593-26-1; **16**, 51593-18-1; **17**, 51593-27-2; **18**, 51593-29-4; 1,2,3-trimethylguanidine hydriodide, 51593-30-7.

References and Notes

(1) Part III: J. E. Oliver and J. L. Flippen, *J. Org. Chem.*, **39**, 2233 (1974).

(2) J. E. Oliver and R. T. Brown, *J. Org. Chem.*, **39**, 2228 (1974).

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(6) The exocyclic thiocarbonyl groups influence the lengths of the dithiazole S-S bonds (see ref 13). We cannot presently assess whether the two thiocarbonyls of **3** influence the S-S bond length twice as much as the single thiocarbonyls influence the S-S bond lengths of **4** and **5**.

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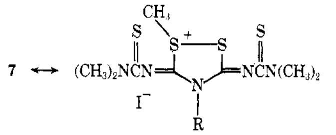
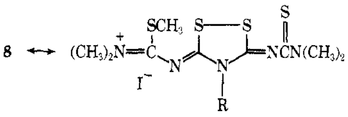
(8) J. E. Oliver and A. B. DeMilo, *J. Org. Chem.*, **39**, 2225 (1974).

(9) A referee has suggested that structures **7** and **8** each show the same bond flipping with respect to **3**, with the same S-S bond broken and the same new S-S bond formed in either case. Thus, he contends, the course of the reaction (*i.e.*, the alkylation of **3**) cannot be diagnostic for no-bond resonance in the starting material. Our feeling is that had **8** been the observed alkylation product, this assessment would have been correct. However, structures **7** and **8**, as they appear in Scheme I, are after the fact (*i.e.*, allowing no-bond interactions) resonance structures of **7a** and **8a**. In the absence of no-bond interactions, **7a** and **8a** are the alkylation products that would have to be considered, and **8a** would be the expected product. The fact is that a ring sulfur, and not a thione sulfur, was alkylated; thus it seems imperative to assume that the course of the reaction was indeed influenced by no-bond interactions.

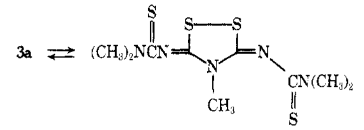


7a



8a

(10) In the solid state, all four sulfurs of **3a** are collinear (ref 3 and 4), and the inner sulfurs are clearly less accessible than the thiocarbonyl sulfurs. In solution, isomerization around a C=N bond could occur (**3a** → **26**); this would help to expose a ring sulfur but it appears unlikely that it would completely reverse the relative accessibilities of the two sulfurs.



26

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(16) Melting points are uncorrected. Nuclear magnetic resonance spectra were recorded on a Varian T-60 spectrometer and infrared spectra were recorded on a Perkin-Elmer Model 137 Infracord. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

(17) Mention of a proprietary product or company does not imply endorsement by the U. S. Department of Agriculture.

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Keto-Enol Tautomerism in the Thiophene Analogs of Anthrone. III. Synthesis and Properties of 4,8-Dihydrobenzo[1,2-*c*:4,5-*c*′]dithiophen-4-one

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The remaining member, 4,8-dihydrobenzo[1,2-*c*:4,5-*c*′]dithiophen-4-one (**11**), of the thieno analogs of anthrone-anthrol has been synthesized from the known 1,3-dichloro-4,8-dihydrobenzo[1,2-*c*:4,5-*c*′]dithiophene-4,8-dione (**15**) by reduction of one of the carbonyl groups to the ketol **16** followed by replacement of the hydroxyl group and subsequent dechlorination of the dichloro ketone **17** by means of copper in boiling propionic acid. Nuclear magnetic resonance, infrared, and ultraviolet spectroscopy indicated the presence of only the keto tautomer **11**. Interaction of **11** with potassium *tert*-butoxide followed by reaction with deuterium oxide results in the replacement of one of the methylene group hydrogen atoms by deuterium; 4,9-dihydronaphtho[2,3-*c*]thiophen-4-one (**22**) behaved similarly and incorporated deuterium. Similar treatment of 4,8-dihydrobenzo[1,2-*c*:4,5-*c*′]dithiophene (**20**), 3,3′-dithienylmethane (**21**), and 3-benzylthiophene gave no evidence of anion formation.

If both of the benzene rings in 9-anthrone are replaced by thiophene nuclei, six analogous keto-enol systems **1-12** result (Table II). The syntheses of the systems **1-10** were reported in a recent publication[1a] and the present report describes the synthesis and some of the properties of the remaining member of the series, **11**.

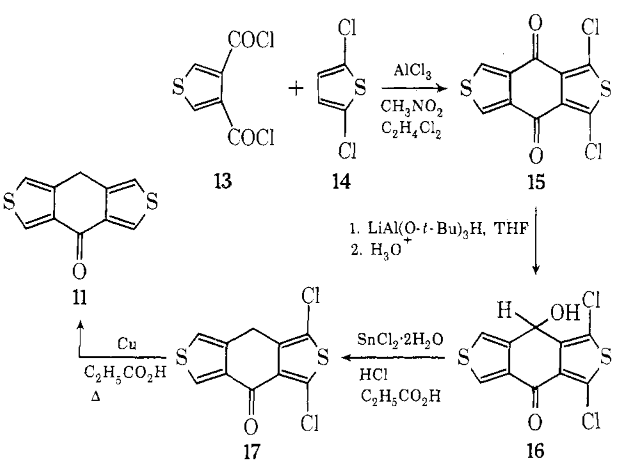
A spectroscopic examination of the position of the keto-enol equilibria in the systems **1-10** showed that the mode of fusion of the thiophene nucleus controls the preferred tautomer that is observed experimentally. A rough correlation was obtained relating the free-energy difference between the keto and enol forms of 1–10 and the observed equilibrium position for each system (Table II).[1a] When at least one thiophene nucleus is *b*-fused as in compounds **1–6**, the enol tautomer tends to be preferred relative to anthrone–anthrol. *c*-Fusion of one thiophene nucleus favors the keto tautomer in systems **7–10**.

As indicated from the calculated ΔDE values in Table II, the di-*c*-fused system **11–12** was predicted to favor the keto form to the greatest extent of all the systems listed. Dominance of the keto form **11** was also indicated owing to the necessity of tetracovalent sulfur participation in the enol form **12**.

Synthesis of 4,8-Dihydrobenzo[1,2-*c*:4,5-*c*′]dithiophen-4-one (11). Attempts to introduce an oxygen function into the bridgehead position of 4,8-dihydrobenzo[1,2-*c*:4,5-*c*′]dithiophene[2] (**20**) *via* oxidation with selenium dioxide resulted in immediate decomposition of the starting material. Treatment of **20** with *N*-bromosuccinimide resulted in nuclear as well as methylene bromination, thus necessitating abandonment of carbonyl introduction at C_4 *via* dimethyl sulfoxide.

The desired compound was ultimately obtained by means of the synthetic scheme outlined below (Scheme I).

Scheme I



The synthesis of 1,3-dichloro-4,8-dihydrobenzo[1,2-*c*:4,5-*c*′]dithiophene-4,8-dione (**15**) as reported by MacDowell and Wisowaty[2] was significantly improved (80% yield as compared to 50%) by modification of the Friedel–Crafts catalyst. Addition of 1 equiv of nitromethane was found to lessen the decomposition of the 2,5-dichlorothiophene (**14**) before the desired ring-closure step had occurred. Reduction of one carbonyl group of the symmetrical dione **15** to the ketol **16** was readily accomplished in 72% yield using lithium tri-*tert*-butoxyaluminum hydride. This reducing agent has been used previously to effect partial reduction of a symmetrical aliphatic dione.[3] The dichlorodione was used at this stage in order to ensure a homogeneous reaction medium owing to the low solubility of the dechlorinated dione, 4,8-dihydrobenzo[1,2-*c*:4,5-*c*′]dithiophene-4,8-dione in nearly all common solvents. The keto **16** was readily separated from unreacted dione by chromatography on neutral alumina, in yields of 70–74%.

After a number of unsuccessful attempts to form the mesylate or tosylate of **16**, which should be reducible by means of sodium cyanoborohydride,[4] the ketol was successfully reduced with stannous chloride in propionic acid saturated with hydrogen chloride to the ketone **17** in yields of 60–74%. Use of propionic acid permitted a homogeneous reaction medium as well as a lower reaction temperature (−12°) than is possible with the previously used acetic acid solvent[5] (15°). Dechlorination of the ketone **17** with copper dust[6] in refluxing propionic acid was achieved in yields of 60–73%. A long reaction time (45 hr) was necessary in order to remove the less labile C_1 chlorine atom. When the progress of the reaction was followed by means of nmr spectroscopy, it was found that the C_3 chlorine atom had been completely removed after 3 hr duration.

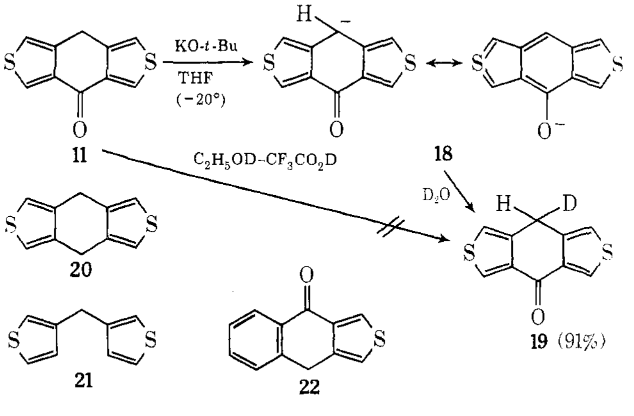
Keto–Enol Tautomerism. The nmr spectrum was recorded for the system **11–12** in the enol-stabilizing solvent Polysol-*d*, as well as in benzene-d_6 with and without added acid (CF_3CO_2H). No changes in the spectrum in the latter case were observed even after 6 days. The spectra in both solvents were consistent with the presence of only the keto form **11** (Table I).

The ir spectrum of **11–12** showed no evidence of OH absorption. The ultraviolet spectrum of **11–12** was also consistent with the keto tautomer, the molar absorptivity being of the expected magnitude. It is seen that the anthrone–anthrol analogs fall into two distinct groups, those containing two *b*-fused thiophene rings (**1–6**) and those containing at least one *c*-fused thiophene ring (**7–8**, **9–10**, **11–12**) (Table II).

Interaction of 4,8-Dihydrobenzo[1,2-*c*:4,5-*c*′]dithiophen-4-one with Base. In an attempt to study possible base-catalyzed enolization of **11**, a cold (−20°) solution of freshly sublimed potassium *tert*-butoxide (10% excess) in THF was added to a cold (−20°) solution of the ketone **11**. A deep black solution was immediately produced and after 2 min a large excess (38 times) of deuterium oxide in dry THF was added. Following acidification, the deuterated ketone **19** was isolated and purified by sublimation, owing to significant loss (50%) of the initially incorporated deuterium when purification was attempted by chromatography on silica gel or neutral alumina. Deuterium incorporation was determined by nmr analysis.

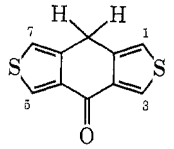
Attempts to induce acid-catalyzed enolization of **11** using C_2H_5OD–CF_3CO_2D at 65° for 3 hr resulted in recovery of starting material with no evidence of any incorporation of deuterium (Scheme II).

Scheme II



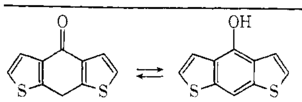
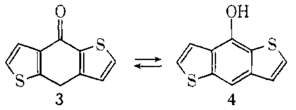
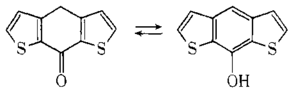
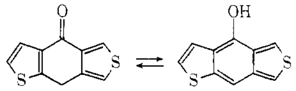
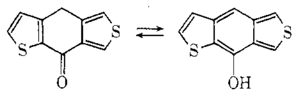
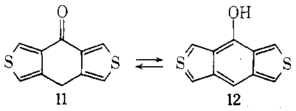
Attempts to alkylate the anion **18** with dimethyl sulfate were unsuccessful. Other *c*-fused ketones in the series were subjected to similar reaction with potassium *tert*-butoxide followed by reaction with deuterium oxide. In the case of 4,9-dihydronaphtho[2,3-*c*]thiophen-4-one (**22**)[1b] deuterium was incorporated in the methylene position (70% monodeuteration). The ketones 4,8-dihydrobenzo[1,2-*b*:4,5-*c*′]dithiophen-4-one (**7**) and 4,8-dihydrobenzo[1,2-*b*:4,5-*c*′]dithiophen-8-one (**9**) proved to be so re-

Table I



Solvent	Proton	Chemical shift, δ
Polysol-*d*	8	4.16 (t, 2 H), $J_{1,8}$ = 1.4 Hz
	1,7	7.16–7.30 (doublet of triplets, 2 H), $J_{1,8}$ = 1.4, $J_{1,3}$ = 3 Hz
	3,5	8.35 (d, 2 H), $J_{1,3}$ = $J_{5,7}$ = 3 Hz
Benzene-d_6	8	3.45 (t, 3 H), $J_{1,8}$ = 1.4 Hz
	1,7	6.36–6.53 (doublet of triplets, 2 H), $J_{1,8}$ = 1.4, $J_{1,3}$ = 3 Hz
	3,5	8.13 (d, 2 H), $J_{1,3}$ = $J_{5,7}$ = 3 Hz
Benzene-d_6 and CF_3CO_2H	8	3.36 (t, 2 H), $J_{1,8}$ = 1.4 Hz
	1,7	6.36–6.46 (doublet of triplets, 2 H), $J_{1,8}$ = 1.4, $J_{1,3}$ = 3 Hz
	3,5	8.10 (d, 2 H), $J_{1,3}$ = $J_{5,7}$ = 3 Hz

Table II

	Tautomer	ΔDE(β)[a]	λ_{max}, mμ[b]	ε
 1 ⇄ 2	Enol	0.80	252	66,500[a]
 3 ⇄ 4	Enol	0.76	253	51,100[a]
 5 ⇄ 6	Enol	0.72	253	61,600[a]
 7 ⇄ 8	Keto	0.53	279	13,700[a]
 9 ⇄ 10	Keto	0.49	303	15,900[a]
 11 ⇄ 12	Keto	0.21	286	17,400

[a] Reference 1a. [b] In 95% ethanol.

active that, even when the reaction with base was carried out very rapidly at low temperatures, only highly colored material was isolated from which no sublimable material could be obtained.

In order to study the enhancement of the acidity of the methylene group in 11 by the carbonyl group, 4,8-dihydrobenzo[1,2-*c*:4,5-*c*′]dithiophene[2] (20), 3,3′-dithienylmethane[7] (21), and 3-benzylthiophene were treated with potassium *tert*-butoxide followed by deuterium oxide as above. Even under more rigorous conditions, longer periods of time, and high temperatures (25°), no deuterium incorporation was observed, starting material being recovered in each case.

Experimental Section[8]

Synthesis of 4,8-Dihydrobenzo[1,2-*c*:4,5-*c*′]dithiophen-4-one (11). A. 1,3-Dichloro-4,8-dihydrobenzo[1,2-*c*:4,5-*c*′]dithiophene-4,8-dione (15). A stirred suspension of thiophene-3,4-dicarboxylic acid (21.5 g, 0.125 mol) in purified thionyl chloride[9] (40 ml) was maintained at reflux for 45 min. The solution was cooled to 30° and the excess thionyl chloride was removed under reduced pressure. The residue was dissolved in dry 1,2-dichloroethane (110 ml) and the remaining thionyl chloride was removed by codistillation. The resulting tan solid was dried *in vacuo* for 1 hr.

To a filtered solution of aluminum chloride (35.1 g, 0.263 mol) and dry nitromethane[10] (16.0 g, 0.263 mol) in dry 1,2-dichloroethane (225 ml) was rapidly added a solution of the acid chloride obtained above in dry 1,2-dichloroethane (150 ml). The resulting solution was stirred for 15 min and 2,5-dichlorothiophene (19.1 g. 0.125 mol) was rapidly added by means of a syringe. The red-brown mixture was then heated to 50–53° for 18 hr; a slow nitrogen flow was maintained to remove the evolved hydrogen chloride. The mixture was then cooled to 10° and 6 *M* hydrochloric acid (250 ml) was added. Chloroform (500 ml) was added and the mixture was shaken vigorously to dissolve all solids. The layers were separated and the aqueous phase was extracted with chloroform (2 × 200 ml). The combined organic layers were washed with saturated sodium bicarbonate solution (250 ml), then dried ($MgSO_4$) and evaporated. The impure ketone which remained was dissolved in a minimum amount of warm chloroform (500 ml) and was chromatographed on a neutral alumina column (4 × 28 cm) using warm chloroform. An initial green fraction was discarded followed by a yellow fraction, which contained 29.0 g (80.0%) of the diketone: mp 214–216°; ir (KBr) 1670 cm^{-1} (C=O); nmr (CF_3COOH) δ 8.60.[2]

B. 8-Hydroxy-1,3-dichloro-4,8-dihydrobenzo[1,2-*c*:4,5-*c*′]dithiophen-4-one (16). To a stirred solution of 1,3-dichloro-4,8-dihydrobenzo[1,3-*c*:4,5-*c*′]dithiophene-4,8-dione (12.05 g, 0.0417 mol) in dry (distilled from lithium aluminum hydride) tetrahydrofuran (900 ml) was added dropwise a solution of lithium tri-*tert*-butoxyaluminum hydride (10.60 g, 0.0417 mol) over a period of 1.5 hr. The reaction mixture was stirred for an additional 3 hr and the tetrahydrofuran was removed under reduced pressure at room temperature. The resulting residue was dried *in vacuo* for 15 min, and chloroform (300 ml) and 3 *M* sulfuric acid (150 ml) were added. The layers were separated and the aqueous layer was extracted with chloroform (3 × 75 ml). The combined organic layers were washed with water (3 × 100 ml) and saturated sodium bicarbonate (100 ml), dried ($MgSO_4$), and evaporated. The impure alcohol was dissolved in a minimum amount of chloroform (125 ml) and chromatographed on a column (3.5 × 20 cm) of neutral alumina. Elution with chloroform provided 8.97 g (74%) of tan needles. Recrystallization from benzene afforded an analytical sample: mp 167–168°; ir (KBr) 3405 (OH), 1645 cm^{-1} (C=O); nmr (DMSO-d_6) δ 5.51 (s, 1 H, -OH), 5.63 (s, 1 H, C_8 hydrogen), 7.80 (d, 1 H, $J_{5,7}$ = 4 Hz, C_7 hydrogen), 8.41 (d, 1 H, $J_{5,7}$ = 4 Hz, C_5 hydrogen).

Anal. Calcd for $C_{10}H_4Cl_2O_2S_2$: C, 41.25; H, 1.39; Cl, 24.35; S, 22.02. Found: C, 41.14; H, 1.42; Cl, 24.26; S, 21.94.

C. 1,3-Dichloro-4,8-dihydrobenzo[1,2-*c*:4,5-*c*′]dithiophen-4-one (17). Propionic acid (30 ml) was flushed with dry nitrogen for 15 min, then stannous chloride dihydrate (4.48 g, 0.020 mol) was added, and the slurry was saturated with hydrogen chloride. After most of the stannous chloride had dissolved, the solution was cooled to −12° in an ice-salt bath. With vigorous stirring a solution of 8-hydroxy-1,3-dichloro-4,8-dihydrobenzo[1,2-*c*:4,5-*c*′]dithiophen-4-one (1.446 g, 0.00497 mol) in propionic acid (240 ml) was added over a period of 45 min at such a rate that the temperature of the mixture was maintained at −15 to −10°. The resulting green mixture was stirred for an additional 1.25 hr and was then poured into ice-water (400 g) containing Filter aid (2 g). The solids were collected by filtration and dried overnight *in vacuo*. The dry residue was extracted with hot chloroform (4 × 100 ml), and the extract was evaporated to afford 1.08 g of impure ketone.

The aqueous filtrate from above was extracted with chloroform (5 × 150 ml) and the combined organic layers were washed with water (5 × 250 ml), saturated sodium bicarbonate (4 × 250 ml), and water (250 ml), dried ($MgSO_4$), and evaporated to afford an additional 0.195 g of impure ketone.

The combined ketone residues were dissolved in chloroform and chromatographed on a column (2 × 19 cm) of neutral alumina. Elution with chloroform provided 1.005 g (74%) of tan leaves. Recrystallization from 1:1 benzene-hexane afforded an analytical sample: mp 188–189°; ir (KBr) 1660 cm^{-1} (C=O); nmr (CF_3COOH) δ 3.86 (d, 2 H, -CH_2), 7.20 (m, 1 H, C_7 hydrogen), 8.38 (d, 1 H, $J_{5,7}$ = 3 Hz, C_5 hydrogen).

Anal. Calcd for $C_{10}H_4Cl_2OS_2$: C, 43.65; H, 1.46; Cl, 25.77; S, 23.30. Found: C, 43.72; H, 1.26; Cl, 26.04; S, 23.15.

D. 4,8-Dihydrobenzo[1,2-*c*:4,5-*c*′]dithiophen-4-one (11). To propionic acid (30 ml) that had been flushed with dry nitrogen was added 1,3-dichloro-4,8-dihydrobenzo[1,2-*c*:4,5-*c′*]dithiophen-4-one (2.87 g, 0.0104 mol) and active copper dust[6] (5.30 g, 0.0835 mol). With vigorous mechanical stirring and a slow nitrogen flow through the system, the reactive mixture was held at reflux for 45 hr and cooled to room temperature and the deep green mixture was added to chloroform (150 ml).

Water was added (150 ml) and the acid was neutralized by addition of sodium bicarbonate. The layers were separated and the aqueous layer was extracted with chloroform (5 × 50 ml). The combined organic layers were dried ($MgSO_4$) and evaporated. The crude ketone which remained was dissolved in a minimum amount of chloroform and chromatographed on a column (2 × 34 cm) of neutral alumina. Elution with chloroform provided 1.57 (g (73%) of peach-colored plates. Recrystallization from 1:1 benzene–hexane provided an analytical sample: mp 133–135°; uv max (95% C_2H_5OH) 286 mμ (ϵ 17,400); ir (KBr) 1640 cm^{-1} (C═O); nmr ($CDCl_3$) δ 4.15 (t, 2 H, $-CH_2-$), 7.10–7.23 (m, 2 H, C_1 and C_7 hydrogen), 8.31 (d, 1 H, $J_{1,3} = J_{5,7} = 3$ Hz, C_3 and C_5 hydrogen).

Anal. Calcd for $C_{10}H_6OS_2$: C, 58.23; H, 2.93; S, 31.09. Found: C, 57.98; H, 2.86; S, 30.84.

E. Deuteration of 4,8-Dihydrobenzo[1,2-*c*:4,5-*c′*]**dithiophen-4-one (11).** To dry (distilled from lithium aluminum hydride) tetrahydrofuran (25 ml) was added 4,8-dihydrobenzo[1,2-*c*:4,5-*c′*]dithiophen-4-one (0.30 g, 0.00145 mol). With vigorous stirring, the solution was flushed with dry nitrogen for 20 min and cooled to −20°. A solution of freshly sublimed potassium *tert*-butoxide (0.179 g, 0.00159 mol) in dry tetrahydrofuran (10 ml) was then rapidly added in one portion. The black reaction mixture was stirred for an additional 2 min and deuterium oxide (1 ml, 0.055 mol) dissolved in dry tetrahydrofuran (5 ml) was rapidly added with a syringe. The reaction mixture was allowed to warm to 2° during a 10-min period, and was then added to ice-cold 1 *M* HCl (20 ml). The red-orange slurry was extracted with chloroform (5 × 20 ml), and the combined organic layers were washed with water (50 ml), dried ($MgSO_4$), and evaporated. Sublimation of the crude residue afforded 0.090 g (30% recovery) of the ketone, mp 131–134°. Nmr analysis indicated 91% monodeuteration at the methylene position.

F. Deuteration of 4,9-Dihydronaphtho[2,3-*c*]**thiophen-4-one (22).** To a solution of 4,9-dihydronaphtho[2,3-*c*]thiophen-4-one (0.4 g, 0.002 mol) in dry THF (20 ml) cooled to −19° under dry nitrogen was rapidly added with vigorous stirring a solution of potassium *tert*-butoxide (0.24 g, 0.0022 mol) in dry THF (10 ml). The violet reaction mixture was stirred for an additional 2 min and deuterium oxide (1 ml. 0.055 mol) in THF (5 ml) was added rapidly. The reaction mixture was allowed to warm to 0° during a 4-min period and was then quenched with ice-cold HCl. Extraction of the red-orange mixture with ether followed by sublimation of the solid residue obtained upon evaporation afforded 0.066 g (16% recovery) of the ketone, mp 104–106°. Nmr analysis indicated 70% monodeuteration at the methylene position.

G. Attempted Deuteration of 4,8-Dihydrobenzo[1,2-*c*:4,5-*c′*]**dithiophene (20).** Similar treatment of the above compound (0.194 g, 0.00101 mol) in THF (7 ml) at 25° with a solution of potassium *tert*-butoxide (0.124 g, 0.0011 mol) in THF (10 ml) for 4 min followed by addition of deuterium oxide (1 ml, 0.055 mol) and work-up as before gave only starting material (0.119 g, 61% recovery). Nmr analysis indicated no deuterium incorporation.

Registry No.—2, 31936-80-8; **4,** 31936-82-0; **6,** 31936-81-9; **7,** 31981-26-7; **9,** 31936-79-5; **11,** 51472-74-3; **13,** 33527-26-3; **14,** 3172-52-9; **15,** 33527-28-5; **16,** 51472-75-4; **17,** 51472-76-5; **19,** 51540-10-4; **22,** 31926-65-5; **22-*d*,** 51472-77-6.

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Photochemical Reactions of 2-Acylthiophenes, -furans, and -pyrroles with Alkenes

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Irradiation of 2-acetylthiophene with tetramethylethylene or isobutene resulted in [4 + 2] addition of the thiophene to the alkene as the major process, as well as a [2 + 2] ring adduct and an oxetane as the minor products, a revision of our earlier structural assignments. 2-Benzoylthiophene and tetramethylethylene on irradiation lead to efficient oxetane formation. 2-Acetylfuran with both olefins mentioned above gave only products of [2 + 2] addition to the ring, in addition to minor amounts of oxetanes. 2-Benzoylfuran and 1-methyl-2-benzoylpyrrole gave only oxetanes or their decomposition products. Triplet excited states of the ketones appear to be intermediates in the formation of at least some of the observed products.

The photochemical behavior of aryl and aryl alkyl ketones has received much scrutiny in the past decde and a half.[1] A fairly clear picture is now available of the factors governing the various transformations of excited states of these carbonyl compounds, including reduction to pinacols,[2] [2 + 2] cycloaddition to olefins leading to oxetanes,[3] and Norrish type II elimination.[4] One structure–reactivity correlation which has emerged is that, in the case of those ketones whose lowest n, π^* triplet state is of an energy similar to or lower than that of the lowest π, π^* triplet, the former species, having considerable odd-electron character on the carbonyl oxygen atom, readily undergoes the transformations mentioned above. Those ketones whose lowest triplet is of predominantly $\pi \rightarrow \pi^*$ character, *e.g.*, naphthyl ketones or 4-biphenylyl ketones, are far less reactive photochemically.

We recently reported in preliminary form some of our results on photochemical cycloadditions of acyl derivatives of thiophene, furan, and pyrrole.[5] The structures of some previously unidentified minor products have now been elucidated; in addition, two of the structural assignments in our earlier report have been found to be incor-