Conversion of α-Hydroxy Ketones to 1,2-Dithiete, *p*-Dithiin, and 1,2-Dithiole Radical Cations[1,2]

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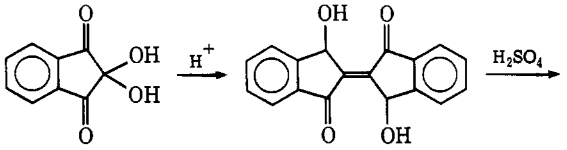
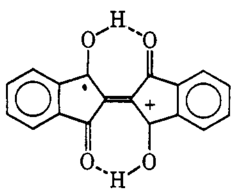
Abstract: α-Hydroxy ketones, or less effectively α diketones, are converted by a mixture of sodium sulfide (or alternately sodium thiosulfate or sodium dithionite) and sulfuric acid to the 1,2-dithiete radical cations (*e.g.*, **9**), identified by esr spectroscopy. Hyperfine splitting by hydrogen atoms α to the spin label have been detected as well as ^{13}C hyperfine splitting at the unsaturated and α carbon atoms.

We have previously reported that α diketones in sulfuric acid solution to which sodium dithionite ($Na_2S_2O_4$) has been added yield stable radical cations.[3–5] Ninhydrin (**1**) upon treatment with sulfuric acid gives a weak esr signal ascribed to **3**. A much stronger signal of **3** is obtained by treatment of **2** (or the corresponding tetraketone, 1,1′,3,3′-tetraketo-$\Delta^{2,2'}$-biindan[5]) with sulfuric acid,[4,5] or by the treatment of ninhydrin with sulfuric acid and a reducing agent such as sodium sulfite, sodium dithionite, or ferrous sulfate.[4] The radical anion **4** can be prepared from **2** (or from the tetraketone[5]) upon treatment with propiophenone enolate anion in dimethyl sulfoxide solution.

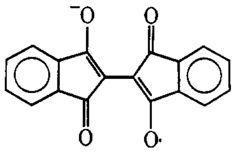


1 **2**



3

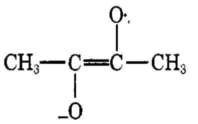
a^H = 1.14 (2, exchangeable in D_2SO_4), 0.92 (4, *o*-H), 0.25 (4, *m*-H) G



4

a^H = 0.45 (4), 0.34 (4) G

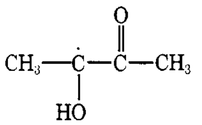
When **3** and **4** are compared it is noted that Σa^H is greater for the radical cation (4.7 G) than for the radical anion (3.2 G). This behavior is quite characteristic of quinone radical anions and hydroquinone radical cations.[5,6] It was surprising that treatment of biacetyl with sulfuric acid and $Na_2S_2O_4$ yielded a species with a^H = 2.17 (6) G whereas the biacetyl radical anion (**5**) in DMSO has a^H = 7.2 (cis) and 5.6 (trans) G.[7] Moreover, the 3-hydroxy-2-butanone radical is known[8,9] and values of a^H = 13.36 (3), 2.57 (3), 2.05 G have been assigned in isopropyl alcohol solution to this species. In view of the values of the hyperfine splitting constant (hfsc) in **5** and **6** the assignment of the $a_{CH_3}{}^H$ = 2.17 G for **7** is perplexing. A solution to this dilemma became apparent when a recent publication assigned values of a^H = 2.06 G to **8** in sulfuric acid.[10] Indeed, we now report that in sulfuric acid solutions of sodium dithionite, sodium thiosulfate, or sodium sulfide (but not sodium sulfite,) α-hydroxy ketones are preferred to the α diketones as precursors. The reaction sequence appears to involve the following steps:



$CH_3{-}C(O\cdot){=}C(O^-){-}CH_3$

5

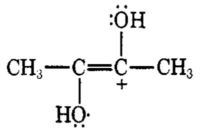
$a_{CH_3}{}^H$ = 5.6 (6) G



$CH_3{-}\dot{C}(HO){-}C(=O){-}CH_3$

6

$a_{CH_3}{}^H$ = 13.36, 2.57 G



$CH_3{-}C(\ddot{O}H){=}\overset{+}{C}(H\ddot{O}\cdot){-}CH_3$

7

$$[CH_3C(\ddot{S}H){=}C(\ddot{S}H)CH_3]^+$$

8

$$Na_2S \text{ or } Na_2S_3O_3 \text{ or } Na_2S_2O_4 \xrightarrow{H_2SO_4} H_2S$$

$$H_2S + RCOCH(OH)R \rightleftharpoons RC(OH)(SH)CH(OH)R \rightleftharpoons$$

$$RC(SH){=}C(OH)R \rightleftharpoons RCH(SH)COR \overset{H_2S}{\rightleftharpoons}$$

$$RCH(SH)C(OH)(SH)R \longrightarrow$$

$$RC(SH){=}C(SH)R \xrightarrow[\text{(oxidation)}]{H_2SO_4} \text{radical cation}$$

It is known that hydrogen sulfide will convert ketones to thioketones. Futhermore, mercaptans react with

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[1] Application of Electron Spin Resonance Spectroscopy to Problems of Structure and Conformation. XXVI.

[2] This work was supported by a grant from the National Science Foundation.

[3] G. A. Russell, E. R. Talaty, and M. C. Young, *J. Phys. Chem.*, **70**, 1321 (1966).

[4] G. A. Russell and M. C. Young, *J. Amer. Chem. Soc.*, **88**, 2007 (1966).

[5] G. A. Russell and F. A. Neugebauer, *Org. Magn. Resonance*, **1**, 125 (1969).

[6] J. R. Bolton and A. Carrington, *Proc. Chem. Soc.*, 385 (1961).

[7] G. A. Russell and R. D. Stephens, *J. Phys. Chem.*, **70**, 1320 (1966).

[8] R. O. C. Norman and R. J. Pritchett, *J. Chem. Soc. B*, 378 (1967).

[9] P. B. Ayscough and M. C. Brice, *ibid.*, 491 (1971).

[10] G. N. Schrauzer and H. N. Rabinowitz, *J. Amer. Chem. Soc.*, **92**, 5769 (1970).

Table I. Comparison of Hyperfine Splitting Constants in Cyclic Semidione Radical Anions and Dithiete Radical Cations at 25°

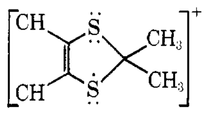
R	a^H		Ratio a_{9a}^H/a_{10}^H
	9a, H_2SO_4	**10**, DMSO[a]	
$(CH_2)_3$	5.37 (4)	14.16 (4)	0.38
$(CH_2)_4$	3.04 (4)	9.82 (4)	0.31
$C(CH_3)_2(CH_2)_3$	2.94 (2)	9.74 (2)	0.30
$C(CH_3)_2CH_2C(CH_3)_2CH_2$	2.62 (2)	8.94 (2)	0.29
$CH(CH_3)(CH_2)_3$	3.57, 3.36, 2.63	10.6, 10.6, 8.3	0.34, 0.32, 0.32
$CH_2CH(CH_3)CH_2CH_2$	3.76 (2), 2.30 (2)	12.33 (2), 7.34 (2)	0.30, 0.31
$CH_2CH((CH_3)_2CH)CH_2CH_2$	3.95 (2), 2.16 (2)	12.63 (2), 7.02 (2)	0.31, 0.31
$CH_2CH((CH_3)_3C)CH_2CH_2$	4.04 (2), 2.02 (2)	13.02 (2), 6.64 (2)	0.31, 0.30
$(CH_2)_5$	2.80 (2), 0.85 (2)	6.60 (2), 2.05 (2)	0.42, 0.43
$(CH_2)_8$	2.34 (2)	8.33 (2)	0.38

[a] Reference 13.

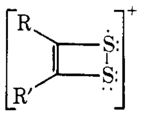
benzoin and acid to form the α-alkylmercapto ketone[11] or the α,α′-dialkylmercaptostilbene.[12]

$$\mathrm{ArCOCH(OH)Ar + RSH \xrightarrow{H^+} ArCH(SR)COAr \xrightarrow[H^+]{RSH} ArC(SR){=}C(SR)Ar}$$

The surprisingly low value of $a_{CH_3}^H$ reported for **8** is not consistent with Hückel MO calculations which incidently work quite well for **5**. Moreover, the values of $a_{CH_3}^H$ observed for **8a** of 6.15 G,[10] as well as a considerable g value difference for the species $a_{CH_3}^H$ = 2.17 and 6.15 G ($\Delta g = 0.006$),[10] has led us to propose **9** as the structure of this intermediate. Indeed, bis(trifluoromethyl)-1,2-dithiete when dissolved in sulfuric acid (an oxidizing agent) yielded a radical cation directly.

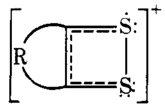


8a

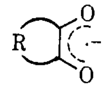


9

In Table I are listed the hfsc of a series of radical cations, possibly **9a**, prepared from cyclic α-hydroxy ketones, as well as the corresponding cyclic semidiones (**10**) reported previously.[13]



9a



10

The ratio of a_{9a}^H/a_{10}^H is quite constant for hexene derivatives reflecting a constant half-chair conformation with little change in planarity or spin distribution in the spin label. However, the cyclopentene and cycloheptene derivatives show considerable variation in the value of this ratio, reflecting undoubtedly differences in planarity of the spin label as a function of ring size.

The conformation effects observed for the substituted cyclohexene analogs of **9a** and **10** are identical.[13b] The 4-*tert*-butyl derivatives display hyperfine splitting by pairs of quasi-axial hydrogens (4.04 G in **9a**, 13.02 G in **10**) and quasi-equatorial hydrogen atoms (2.02 G in **9a**, 6.64 G in **10**). The unsubstituted cyclohexene derivatives are rapidly time averaged at 25° so that the average values of a_α^H are 3.04 in **9a** and 9.82 in **10**. The 4-methyl and 4-isopropyl derivatives show less conformational preference than the 4-*tert*-butyl derivative (which we believe is locked in the conformation with the *tert*-butyl group equatorial) but the degree of conformational preference is exactly the same for both spin labels as indicated by the constancy of a_{9a}^H/a_{10}^H. In the cycloheptene analog the larger hyperfine splitting is at the α-axial position and the small splitting at the β-equatorial position.[13c] The constancy of a_{9a}^H/a_{10}^H for these α and β splittings suggests that the magnitude of these splittings is determined completely by the magnitude of spin density of the sp^2 carbon atoms, and that spin density on the oxygen or sulfur atoms is not important in this regard. Unfortunately bicyclic diketones, whose semidiones give a rich long-range hyperfine splitting pattern, failed to form the dithiete radical cations (*e.g.*, camphorquinone) or gave an unresolved spectrum (*e.g.*, bicyclo[2.2.1]heptane-2,3-dione).

Treatment of a series of acyclic acyloins with sulfuric acid and a hydrogen sulfide precursor provided a series of acyclic radical cations. Although in the semidiones cis and trans radical anions are often observed, only a single radical cation was found.

The absence of cis/trans isomers, or a_{SH}^H, or additional species such as $[RC(SH{=}C(OH)R]\cdot^+$, seems more consistent with the dithiete structure **9** or **9a** than the ethylenedithiol structure **8**. In fact, attempts to make radical cations with bulky R groups (where the semidiones exist in a highly preferred trans arrangement) were unsuccessful (R = *tert*-butyl, cyclohexyl, 2,2-dimethylcyclopropyl, 2,2-diphenylethyl).

Hyperfine splitting constants for a series of dialkylthiete radical cations as well as the corresponding cis and trans semidiones (**11**) are given in Table II.

The data of Table II seem to be quite consistent with the assignment of structure **9** to the radical cations. The constancy of $a_9^H/a_{cis\text{-}11}^H$ (Table II) supports this interpretation. The radical cation assigned to **9**, R = R′ = CF_3, requires special comment. Treatment of bis(trifluoromethyl)-1,2-dithiete with a 1:1 mixture of sulfuric acid and nitromethane gave a radical cation with hyperfine splitting by 6 fluorine atoms, a^F = 1.35 G. No reducing agent was required. Since sulfuric acid is itself an oxidizing agent, the dithiete structure **9b** seems definitely to be preferred. The relative values of a^F in **9b** and **11a**[14] are surprising since the

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(11) W. A. Mitchell and S. Smiles, *J. Chem. Soc.*, 1529 (1933).

(12) T. Posner, *Chem. Ber.*, **35**, 506 (1902).

(13) (a) G. A. Russell and E. T. Strom, *J. Amer. Chem. Soc.*, **86**, 744 (1964); (b) G. A. Russell, G. R. Underwood, and D. C. Lini, *ibid.*, **89**, 6623 (1967); (c) G. A. Russell and R. G. Keske, *ibid.*, **92**, 4458 (1970).

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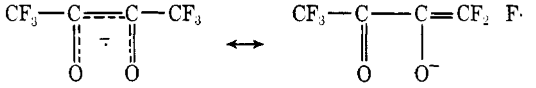
Table II. Hyperfine Splitting Constants for Dithiete Radical Cations (**9**) and Semidione Radical Anions $RC(O\cdot)=C(O^-)R'$ (**11**) at 25°

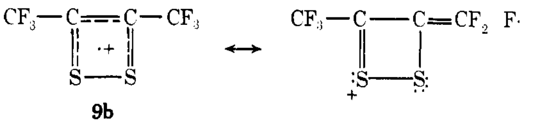
R	R′	a^H, **9**, H_2SO_4	a_{11}^H, DMSO Cis	a_{11}^H, DMSO Trans	$a_9^H/a_{cis\text{-}11}^H$
H	H	2.76 (2)		7.6 (2)	
H	CH_3	3.2 (1), 1.9 (3)	8.7 (1), 7.6 (3)	7.7 (1), 5.1 (3)	0.37
H	$C(CH_3)_3$	3.17 (1)	8.7 (1)	7.8 (1)	0.37
H	C_6H_5	3.14 (1)		6.88 (1)	
CH_3	CH_3	2.17 (6)[a]	7.0 (6)	5.6 (6)	0.31
CF_3	CF_3	1.35 (6)[b,c]	10.9 (6)[b]	8.3 (6)[b]	0.12[b]
$CH_3CH_2CH_2$	$CH_3CH_2CH_2$	2.05 (4)	5.6 (4)	4.6 (4)	0.37
$(CH_3)_3CCH_2$	$(CH_3)_3CCH_2$	1.55 (4)	4.5 (4)	3.50 (4)	0.34
$(CH_3)_2CH$	$(CH_3)_2CH$	1.06 (2)		2.02 (2)	

[a] $g = 2.0155$. [b] a^F. [c] $g = 2.0158$.

ratio is 0.12 instead of the 0.3–0.4 observed for the hydrogen analogs. If the hyperfine splitting is determined mainly by hyperconjugation a possible explanation is that carbon–fluorine hyperconjugation is more important (relative to carbon–hydrogen hyperconjugation) in the radical anion than in the radical cation.

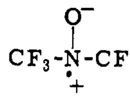


11a



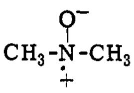
9b

It is well known that the magnitude of carbon–hydrogen hyperconjugation is a function of charge density as well as spin density such that larger values of $a_{CCH_3}^H$ are observed for radical cations than for radical anions.[15] It seems reasonable that the reverse effect would be observed for carbon–fluorine hyperconjugation. In fact this phenomenon is observed in the magnitudes of a^F and a^H in the appropriate nitroxides and ketyls.



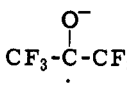
$CF_3{-}\overset{O^-}{\underset{\cdot\,+}{N}}{-}CF_3$

$a^F = 8.2$ G[16]



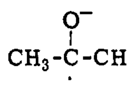
$CH_3{-}\overset{O^-}{\underset{\cdot\,+}{N}}{-}CH_3$

$a^H = 13.4$ G[17]



$CF_3{-}\overset{O^-}{\underset{\cdot}{C}}{-}CF_3$

$a^F = 35$ G[18]



$CH_3{-}\overset{O^-}{\underset{\cdot}{C}}{-}CH_3$

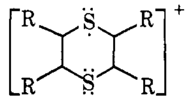
$a^H = 17.3$ G[19]

The esr spectrum of **9** with either $R = C_6H_5$, $R' = H$, or $R = R' = CH_3$ collapsed to a singlet in D_2SO_4. We conclude that hydrogen–deuterium exchange occurs readily at both the sp^2 carbon atom and the adjacent α position in sulfuric acid solution. Whether exchange occurs in the radical cation itself or in the ketonic precursor cannot be specified.

By use of $CH_3{}^{13}C(OSi(CH_3)_3){=}C(OSiC(CH_3)_3)CH_3$ ($\sim$10% ^{13}C enrichment)[20] it was possible to measure $a_{CS}^C = 1.20$ G in **9**.

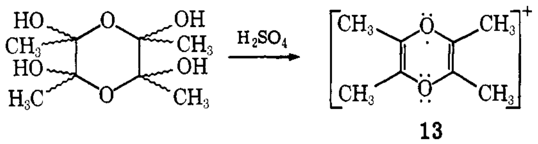
Dimethylsemidione gives $a_{CO}^C = 0.6$ (trans) and 1.15 (cis) G; $a_{CH_3}^C = 4.5$ (cis) and 5.2 (trans) G. The low value of a_{CS}^C in **9** (and **11**) requires a high degree of planarity at the vinyl carbon atom, *i.e.*, the unpaired electron is in an orbital with little s character. The value of $a_{CH_3}^C$ was not determined in **9** but it should be approximately $(0.35)(4.5) = 1.6$ G.

As we originally reported,[3] a second radical species is observed when α-hydroxy ketones or α diketones are treated with a hydrogen sulfide source in sulfuric acid. This by-product gives an esr absorption at higher field than the dithiete radical cation and becomes relatively more important as the sulfuric acid is diluted with water[3] or nitromethane.[10] Schrauzer and Rabinowitz[10] have also observed this species and attributed it to the *p*-dithiin radical cation (**12**) also observed by Lucken.[21] We have observed what we believe to be the oxygen analog **13**.



12

The formation of **12** is not unexpected since benzoin and hydrogen sulfide are known to react to yield the dithiin with $R = C_6H_5$.[22] Radical ion **13** was formed by treatment of acetoin dimer with sulfuric acid. We were unable to detect analogs to **13** with hydrogen atoms in place of the methyl groups by use of glycolaldehyde or lactaldehyde dimers; the parent dioxin molecule is unknown. Table III lists the *p*-dithiin radical cations observed in H_2SO_4 (50%)–CH_3NO_2 (50%).



13

$a^H = 4.06$ (12) G

$a^C = 2.3$ (natural abundance) G

The variations in a_α^H for **12** reflect conformational preferences nearly equal to those in the semidiones as

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(15) R. Hulme and M. C. R. Symons, *J. Chem. Soc.*, 1120 (1965).

(16) P. J. Scheidler and J. R. Bolton, *J. Amer. Chem. Soc.*, **88**, 371 (1966).

(17) G. Chapalet-Letourneux, H. Lemaire, and A. Rassat, *Bull. Soc. Chim. Fr.*, 3282 (1965).

(18) E. G. Janzen and J. L. Gerlock, *J. Phys. Chem.*, **71**, 4577 (1967).

(19) K. Eiben and R. W. Fessenden, *ibid.*, **75**, 1186 (1971).

(20) G. A. Russell, D. F. Lawson, H. L. Malkus, and P. R. Whittle, *J. Chem. Phys.*, **54**, 2164 (1971).

(21) E. A. S. Lucken, *Theor. Chim. Acta*, **1**, 397 (1963); P. D. Sullivan, *J. Amer. Chem. Soc.*, **90**, 3618 (1968).

(22) R. Mayer and M. Nitzschke, *Chem. Ber.*, **96**, 2539 (1963).

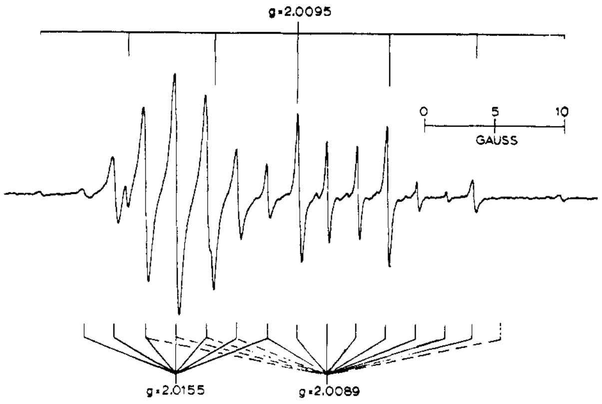


Figure 1. The radical cations observed upon addition of 0.1 mmol of acetoin in 0.5 ml of acetone to 5 ml of a 1:1 mixture of sulfuric acid and nitromethane followed by 1 mmol of sodium sulfide. The first derivative esr spectra are assigned to **9** (g = 2.0155), **12** (g = 2.0089), and **8a** (g = 2.0095).

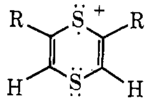
indicated by the constancy of the ratio of $a_\alpha{}^H$ for **12** and cis-**11** (Table III).

Table III. *p*-Dithiin Radical Cations

R	a^H, **12**	$a_\alpha{}^H$, cis-**11**	$\alpha_{12}{}^H/a_{\alpha\text{-cis-11}}{}^H$
H[a]	2.84 (4)[b]		
CH_3	2.11 (12)	7.0 (6)	0.30
C_2H_5	1.58 (8)	6.0 (4)	0.26
$-(CH_2)_3-$	4.75 (8)	14.2 (4)	0.33
$-(CH_2)_4-$	2.92 (8)	9.82 (4)	0.30

[a] g = 2.0089. [b] a^H = 2.82 (4) G, ref 21.

Radical cation **12**, R = CH_3, was prepared with ^{13}C at the vinyl and at the methyl position to give $a_{CS}{}^C$ = 1.4 G and $a_{CH_3}{}^C$ = 1.4 G. For **13** ^{13}C satellites in natural abundance could be detected, a^C = 2.3 G. 1,2-Disubstituted α-hydroxy ketones with bulky substituents failed to yield the dithiin radical cations. *tert*-Butylglycolaldehyde ($(CH_3)_3CCOCH_2OH$) gave a mixture of two dithiin radical cations, perhaps the head-to-head and tail-to-tail dimerization products (a^H = 2.82 (2) and 3.31 (2) G), **14** and **15**, R = *tert*-butyl. In D_2SO_4 (50%)-CH_3NO_2 (50%) complicated spectra were observed from acetoin and 2-hydroxycyclohexanone at the proper g value for the dithiin radical cation. Hydrogen–deuterium exchange at the α position is indicated.



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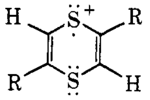

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Using a value of $Q_{CCH_3}{}^H$ = 40 G for radical cations[23] it appears that $\rho_{C\pi}$ is 0.05 for **12** and **9** but 0.15 for **8a**. Hückel MO calculations for **8**, **9**, and **12** were consistent with these empirical observations. Using the parameters $\alpha_S = \alpha_C + 1.0\beta_{CC}$, $\beta_{CS} = 0.566\beta_{CC}$ and $\beta_{SS} = \beta_{CC}$ the values of $\rho_C{}^\pi$ were calculated to be 0.0845 for **9** (five π electrons) and 0.125 for **12** (seven π electrons). As the value of β_{SS} in **9** is decreased to zero (to give **8**) the value of $\rho_C{}^\pi$ increases to 0.25. These calculations are thus in agreement with the assignment of structure **9** rather than **8**, to the species with $a_{CH_3}{}^H$ = 2.17 G, g = 2.0155.

Addition of acetone or methyl ethyl ketone to a mixture of biacetyl and hydrogen sulfide in H_2SO_4 (50%)-CH_3NO_2 (50%) gave in addition to **9** and **12** another radical cation, g = 2.0095 (see Figure 1), previously prepared by Schrauzer and Rabinowitz[10] and assigned the 1,3-dithiole structure.[8a]

Experimental Section

Typical Experimental Preparation of a Dithiete Radical Cation. The diketone or α-hydroxy ketone (0.1 mmol) is dissolved in 5 ml of 98% sulfuric acid. After addition of 1 mmol of sodium sulfide ($Na_2S \cdot 9H_2O$) the resultant solution was transferred to a flat fused-silica esr cell. The esr spectrum could be detected immediately without deoxygenation. The presence of oxygen or colloidal sulfur did not appear to affect the spectra. The spectra were stable for hours at 25°. Cooling the 98% sulfuric acid solutions did not improve resolution. The spectra were not examined at elevated temperatures. To prepare the dithiin radical cations a 1:1 mixture of H_2SO_4 and CH_3NO_2 was used as the solvent. To prepare the 1,3-dithiole radical cations the 1,2 diketone (0.1 mmol) or α-hydroxy ketone in 0.5 ml of acetone or 2-butanone was added to 5 ml of 98% sulfuric acid followed by 1 mmol of sodium sulfide. The spectra were obtained using a Varian E-3 spectrometer. Calibration was achieved by use of a aqueous sample of Fremy's salt in a capillary tube placed inside the esr cell.

Reagents. Glyoxal–sodium bisulfite addition product was a convenient source of the dithiete (g = 2.0155) and *p*-dithiin (g = 2.0089) radical cations. Commercial acetoin (85% in water) was purified by extraction with chloroform. followed by drying over sodium sulfate, and distillation: bp 41° (20 Torr). The ^{13}C-enriched derivatives, $^{13}CH_3COCH(OH)CH_3$ and $CH_3{}^{13}C(OSi(CH_3)_3){=}C(OSiC(CH_3)_3)CH_3$, have been described elsewhere.[20] The bis(trimethylsiloxy)alkene was converted to the acetoin by refluxing 0.2 mmol with 1 drop of hydrochloric acid for 5 min before addition to the sulfuric acid solution. Acetoin dimer was formed from acetoin after storage in a refrigerator for several weeks: mp 95° (lit.[24] mp 95°). The propionoin used had bp 64–67° (15 Torr) (lit.[25] bp 73° (20 Torr)).

Dineopentylacyloin was synthesized by Dr. H. Malkus by the acyloin condensation of 6 g of ethyl 3,3-dimethylbutyrate and 23 g of sodium in xylene at 105–110°. Distillation gave a yellow oil which was purified by glpc and collected as a colorless oil: pmr (CCl_4) δ 4.20 (d × d, J = 9.1, 2.7 Hz, 1), 3.10 (broad s, 1), 2.3 (s, 2), 1.39 (d × d, J = 9.1, 2.7 Hz, 2), 1.02 (s, 18); mass spectrum (60 eV) parent peak at *m/e* 200.

Anal. Calcd for $C_{12}H_{24}O_2$: C, 71.99; H, 12.08. Found: C, 71.92; H, 12.36.

Commercial acetol or pyruvaldehyde gave the same spectra. 1-Hydroxy-3,3-dimethyl-2-butanone was prepared by hydrolysis of 1-bromo-3,3-dimethyl-2-butanone: bp 57° (16 Torr) (lit.[26] bp 52.5° (12 Torr)). 1,2-Cyclopentanedione, mp 55–56° (lit.[27] mp 55–56°), was converted to the cycloalkenedithiol radical cation. 1,2-Cyclohexanedione, α-hydroxycyclohexanone, α-bromocyclohexanone, or α-ethoxycyclohexanone all yielded the same radical cation spectrum. The 2-hydroxy-6-methylcyclohexane, 2-hydroxy-6,6-dimethylcyclohexanone, 2-hydroxy-3,3,6,6-tetramethylcyclohexanone, 2-hydroxy-4-methylcyclohexanone, 2-hydroxy-4-isopropylcyclohexanone, and 2-hydroxy-4-*tert*-butylcyclohexanone have been described previously.

1,2-Cycloheptanedione was prepared: bp 109–112° (18 Torr); $n^{20}D$ 1.4683 (lit.[28] bp 107–109 (17 Torr)); $n^{20}D$ 1.4685). 2-Hydroxycyclodecanone (K and K Laboratories, Inc.) yielded a rather poor signal of the dithiete radical cation. 2-Hydroxycyclobutanone

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was prepared[29] but failed to yield a radical cation. Glycolaldehyde dimer from Aldrich Chemical Co. did not yield a spectrum in sulfuric acid solution. Lactaldehyde dimer was prepared[30] and also failed to yield a signal. Norcamphorquinone gave a weak and uninformative spectrum. No signal could be detected from camphorquinone, glucose, or fructose.

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Trifluoroacetyl Hypohalites as Aromatic Halogenating Agents

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Abstract: Equilibrium constants for formation of trifluoroacetyl hypohalite and trifluoroacetoxymercuric halide from the reactions of iodine and bromine with mercuric trifluoroacetate in trifluoroacetic acid have been determined spectrophotometrically. The kinetics of halogenation of trifluoromethylbenzene and *p*-nitrotoluene in solutions of iodine and mercuric trifluoroacetate have been investigated, and rate constants have been evaluated on the assumption that the actual halogenating agent is trifluoroacetyl hypoiodite. A similar interpretation has been placed on the results of a study of the reaction of nitrobenzene in trifluoroacetic acid solutions of bromine and the mercury salt. From the results of this and earlier studies it has been established that the reactivities of various electrophilic aromatic halogenating agents increase in the order $Br_2 \simeq ICl \simeq CH_3COOI \ll CF_3COOI < CH_3COOBr \ll CF_3COOBr$. Solutions of acetyl hypoiodite have been prepared from the reaction of iodine and silver acetate in acetic acid and the kinetics of iodination of pentamethylbenzene by the hypoiodite so generated have been investigated. The rate constant for the second-order reaction compares favorably with that evaluated previously for the halogenation of pentamethylbenzene in acetic acid solutions of iodine and mercuric acetate.

The reactions of both bromine and iodine with aromatic compounds in the presence of silver trifluoroacetate are known to yield products which are characteristic of electrophilic substitution processes.[1,2] The effective halogenating agent is presumed to be trifluoroacetyl hypobromite or hypoiodite. Because of the inductive effect of the trifluoromethyl group it can be anticipated that these particular hypohalites should be unusually reactive as sources of positive halogen in attacking the aromatic nucleus. The current investigation has been undertaken primarily to compare semiquantitatively the reactivities of these hypohalites with those of structurally related electrophilic aromatic halogenating agents.

It has been demonstrated previously that in acetic acid solutions of mercuric acetate and bromine or iodine equilibria are established as represented in eq 1.[3,4] In

$$Hg(OCOCH_3)_2 + X_2 \rightleftharpoons Hg(OCOCH_3)X + CH_3COOX \qquad (1)$$

such solutions benzene and its methyl substitution products undergo ring halogenation. The kinetics of these reactions have been explained[3,4] on the assumption that in the slow step acetyl hypohalite attacks the aromatic substrate (eq 2 and 3).

$$CH_3COOX + ArH \longrightarrow ArX + CH_3COOH \qquad (2)$$

where

$$-d[X_2]_T/dt = k[ArH][CH_3COOX] \qquad (3)$$

$$[X_2]_T = [X_2] + [CH_3COOX]$$

In connection with the comparative study in question the equilibria for the formation of trifluoroacetyl hypoiodite and hypobromite from mercuric trifluoroacetate and the appropriate halogen in trifluoroacetic (*cf.* eq 1) acid have been investigated. In addition rate constants for reaction of the trifluoroacetyl hypohalites (as generated from the mercuric salts) with various benzene derivatives (eq 3) have been determined.

In a subsidiary study the kinetics of reaction of pentamethylbenzene with acetyl hypoiodite generated through the reaction of silver acetate and iodine in acetic acid have been investigated. The results support the conclusion that eq 3 is the correct rate law for mercuric acetate induced reactions of halogen and aromatic substrates in acetic acid.

Experimental Section

Materials. Commercial samples of bromine, toluene, silver oxide (Mallinckrodt Analyzed Reagent), and pentamethylbenzene (Eastman Organic Chemicals) were used without further purification. Reagent grade iodine (CP Baker) was sublimed before use. Baker and Adamson reagent grade silver acetate was dried at 40° *in vacuo* for 24 hr.

Mallinckrodt glacial acetic acid was refluxed with 2% by volume acetic anhydride for 24 hr and then distilled using a Widmer column. A constant boiling middle fraction (118°) was collected for use in kinetic studies.

Mallinckrodt trifluoroacetic acid was distilled using a Widmer column. A constant boiling middle fraction (72°) was collected and stored in a desiccator before use as a solvent. The water content of this material was less than 0.1% as established by titration with Karl-Fischer reagent.

Nitrobenzene (Eastman Organic Chemicals) was steam distilled from 3 *N* sulfuric acid, washed with distilled water, and dissolved in ether. The dried ether solution was distilled. A constant boiling middle fraction of nitrobenzene was collected at 1.5 mm pressure for use in kinetic studies.

p-Nitrotoluene (Eastman Organic Chemicals) was dissolved in acetone, and the solution was treated with decolorizing carbon.

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