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Organic Sulfur Compounds. X. Co-oxidation of Thiols and Phenylacetylene

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Phenylacetylene and thiols are readily co-oxidized by molecular oxygen at ambient or low temperatures by a radical mechanism. The co-oxidation probably proceeds through vinylic hydroperoxides to yield phenylglyoxal hemithioacetals. The hemithioacetals derived from aliphatic thiols were also synthesized by the oxidation of the corresponding alkylmercaptoacetophenones with hydrogen peroxide–acetic acid. Phenylmercaptoacetophenone yielded ω-phenylsulfinylacetophenone on oxidation at room temperature and ω-phenylmercapto-(acetoxy)-acetophenone at higher temperatures in the presence of acetic anhydride. The structures of phenylglyoxal hemithioacetals and related compounds were characterized by n.m.r. and infrared studies. Infrared established that phenylglyoxal hemithioacetals have intramolecular hydrogen bonding between the OH and CO groups.

Introduction

Co-oxidation of thiols with olefins by molecular oxygen to yield substituted 2-sulfinylethanols has been known for about fifteen years.[3] It was established later[4,5] that the reaction proceeds by a radical mechanism to yield unstable 2-mercaptoethyl hydroperoxide intermediates which rearrange on standing to 2-sulfinylethyl alcohols.

$$(RSH \longrightarrow RS\cdot)$$

$$RS\cdot + CHR'{=}CR''_2 \longrightarrow RS{-}CHR'{-}CR''_2\cdot$$

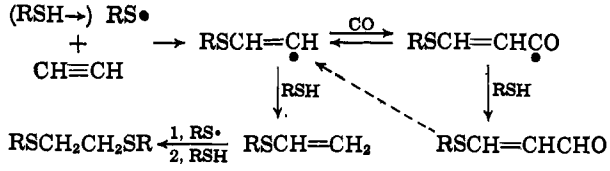
$$RS{-}CHR'{-}CR''_2\cdot + O_2 \longrightarrow RS{-}CHR'{-}CR''_2{-}O_2\cdot$$

$$RS{-}CHR'{-}CR''_2{-}O_2\cdot + RSH \longrightarrow RS{-}CHR'{-}CR''_2{-}O_2H\ (+\ RS\cdot)$$

$$RS{-}CHR'{-}CR''_2{-}O_2H \longrightarrow R{-}SO{-}CHR'{-}CR''_2{-}OH$$

More recently, this co-oxidation reaction has been extended to diolefins.[6-8] The results of these studies suggested that similar reactions of thiols with acetylenes may occur. The examination of phenylacetylene-thiol co-oxidations was also of interest from the viewpoint of the chemistry of vinylic radicals that are expected to be intermediates in these radical type reactions of acetylenes.

A reaction closely related to addition and co-oxidation is the "co-carbonylation" of thiols with ethylene[9] and acetylene.[10] Co-carbonylation of 1-butanethiol and acetylene at 3000 atm. carbon monoxide pressure yielded 17% of 3-*n*-butylmercaptopropenal and 32% of 1,3-bis-butylmercaptoethene, the latter as a by-product.



The large amount of the bis-mercaptoethylene is probably due to the reversibility of the carbonylation reaction.[9,11] A better yield might be expected from the co-oxidation of thiols with acetylenes since the combination of hydrocarbon radicals with oxygen by a similar mechanism is usually a fast, irreversible reaction that does not require a high partial O_2 pressure.[12]

Results

It was found in preliminary experiments that solutions containing benzenethiol and phenylacetylene absorb oxygen readily when exposed to air. The main product of such reactions, however, was the thiol–phenylacetylene monoadduct, 2-phenylmercapto-1-phenylethylene. Apparently there is a competition between the oxygen and the thiol for the intermediate vinylic radical. Therefore, in subsequent experiments the thiol was added dropwise, at a rate parallel to the oxygen absorption, to a stirred solution of phenylacetylene saturated with oxygen. Under these conditions no adduct by-products were observed.

At −75°, oxygen absorption of a phenylacetylene solution containing benzenethiol started without any outside initiation after an induction period of about 5 minutes. At temperatures between −20 and −80°, the reaction yielded an unstable, almost colorless solid. This solid gave a strong positive reaction for a hydroperoxide. When allowed to warm above −10°, it melted and turned into a brown semisolid with the loss of its hydroperoxide content. However, when it was kept at −10°, this intermediate slowly lost its hydroperoxide content without melting and was converted to a compound that is a solid at room temperature. This solid had the same elemental composition as the lower melting peroxidic intermediate.

Elemental analyses, infrared and n.m.r. spectra indicated that the co-oxidation product was a phenylglyoxal-hemithioacetal (Ia), formed by the reaction

$$R{-}SH + HC{\equiv}C{-}Ph + O_2 \longrightarrow R{-}S{-}CH(OH){-}CO{-}Ph \quad (I)$$

a, R = Ph; b, R = CH_3; c, R = CH_3CH_2; d, R = $CH_3CH_2CH_2CH_2$

The reaction can also be carried out at room temperature. Under these conditions, however, no hydroperoxide intermediate can be detected and the yield of final product is lower.

Aliphatic thiols—methane-, ethane- and butanethiol—could also be co-oxidized with phenylacetylene. However, ultraviolet initiation of the reaction was necessary. The products were again crystalline solids. Their elemental analyses, infrared and n.m.r. spectra (Tables I and II, Fig. 1 and 2) suggested that they were the corresponding phenylglyoxal hemithioacetals. Attempts to oxidize these products with H_2O_2–acetic acid resulted in oxidative cleavage to benzoic acid. This was another indication of the phenylglyoxal hemithioacetal structure.

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TABLE I

CHARACTERISTIC INFRARED ABSORPTION PEAKS OF CO-OXIDATION PRODUCTS OF THIOLS AND PHENYLACETYLENE AND RELATED COMPOUNDS

Formula of compound	Characteristic absorption peaks,[a] μ: OH[b]	Stretching region: -C-H	C=O	(C=C)
$C_6H_5SCH(OH)COPh$	*2.9m*	3.25w, 3.4m	*6.0vs,*	6.3s, 6.35m
$C_6H_5SCH(OAc)COPh$		3.25w, 3.4w	*5.7ws, 5.9vs,*	6.35m, 6.4m
$C_6H_5SCH_2COPh$[c]		3.25m, 3.35m, 3.4m	*5.95vs,*	6.2s, 6.3s
$C_6H_5SOCH_2COPh$		3.3w, 3.35m, 3.4m	*5.95vs,*	6.25s, 6.3s
$C_6H_5SO_2CH_2COPh$[d]		3.3w, 3.35m, 3.4m	*5.85vs,*	6.25s, 6.3s
$4\text{-}ClC_6H_4SCH(OH)COPh$[e]	*2.95m*	3.3w, 3.4w	*6.0vs,*	6.25m, 6.35m
$4\text{-}ClC_6H_4SCH_2COPh$[c,f]		3.25w, 3.4w, 3.45m	*5.9vs,*	6.25m, 6.3w
$4\text{-}ClC_6H_4SOCH_2COPh$[g]		3.25m, 3.4w, 3.45m	*5.95vs,*	6.25m, 6.3m
$CH_3SCH(OH)COPh$	*2.9m*	3.3w 3.45m	*6.0vs,*	6.3s, 6.35m
CH_3SCH_2COPh[c,h]		3.25m, 3.35s, 3.4vs	*5.95vs,*	6.25s, 6.3s
$CH_3SO_2CH_2COPh$[i]		3.3w, 3.35w, 3.4m	*5.95vs,*	6.25s, 6.3s
$CH_3CH_2SCH(OH)COPh$	*2.9m*	3.3w, 3.4s, 3.45m	*6.0vs,*	6.25s, 6.3m
$CH_3CH_2SCH_2COPh$[c,j]		3.25m, 3.35s, 3.4s	*6.0vs,*	6.25vs, 6.3m
$CH_3CH_2CH_2CH_2SCH(OH)COPh$	*2.9m*	3.25w, 3.4s, 3.5m	*6.0vs,*	6.25s, 6.3m
$CH_3CH_2CH_2CH_2SCH_2COPh$[c,k]		3.25m, 3.4vs, 3.5s	*6.95vs,*	6.25vs, 6.3vs

Formula of compound	Characteristic absorption peaks,[a] μ: $-CH_2$ and $-CH_3$ deformation region	Fingerprint region (C-O stretching and O-H deformation included)
$C_6H_5SCH(OH)COPh$	6.8w, 6.9s, 6.95s, 7.25s	7.65s *7.9vs* 8.5s 9.2s, 9.4vs, 9.45vs, *9.75m*
$C_6H_5SCH(OAc)COPh$	6.75m, 6.9s 7.3s	7.45m *8.05vs,* 8.2vs, 8.5s 9.55vs, 9.7s
$C_6H_5SCH_2COPh$[c]	6.75s, 6.9s, 6.95s, 7.05w	7.65m *7.85vs* 8.4w *8.8s*
$C_6H_5SOCH_2COPh$	6.9s, 7.05m	7.65m *7.8vs* 8.45m *8.7vs, 9.2s* 9.5vs, *9.7vs*
$C_6H_5SO_2CH_2COPh$[d]	6.85s, 6.9s, 7.1m	*7.6vs,* 7.65vs, *7.8vs,* 8.15s, 8.45m *8.6vs, 8.8s, 9.2s* 9.7m
$4\text{-}ClC_6H_4SCH(OH)COPh$[e]	6.75s, 6.9s 7.2s	7.8m, *8.0vs* 8.5m 8.95m, *9.1vs, 9.2vs*
$4\text{-}ClC_6H_4SCH_2COPh$[c,f]	6.75vs, 6.9s, 7.2m, 7.3s	7.55s *7.8s* 8.3vs *9.1vs*
$4\text{-}ClC_6H_4SOCH_2COPh$[g]	6.75m, 6.9s, 7.2s, 7.4s	7.65s, 7.7s, *7.8s* 8.3s 9.15 9.3s *9.65vs*
$CH_3SCH(OH)COPh$	6.9s, 7.0m, 7.25s	7.6m 7.7m, *8.0vs,* 8.5vs, 8.6s *9.15vs,* 9.3s
CH_3SCH_2COPh[c,h]	6.7s, 6.9vs, 6.95vs, 7.05vs	7.6s *7.8vs,* 8.2m, 8.35s, 8.45s, 8.8w 9.3m 9.6m
$CH_3SO_2CH_2COPh$[i]	6.9s, 7.1m	*7.6vs,* 7.7vs, *7.8vs,* 8.2s, 8.45s, *8.65vs, 8.9vs,* 9.2w 9.7m
$CH_3CH_2SCH(OH)COPh$	6.9s, 6.95m, 7.2s	7.7m, *7.9s, 8.0vs,* 8.4s, 8.45vs *9.15vs,* 9.5s
$CH_3CH_2SCH_2COPh$[c,j]	6.7w, 6.9vs, 7.1s, 7.3s	7.6s *7.9vs* 8.35vs, 8.45s, *8.8s,* 9.1w, 9.3m, 9.5m, 9.7w
$CH_3CH_2CH_2CH_2SCH(OH)COPh$	6.8m, 6.9vs, 7.2s	7.7m, *7.95vs,* 8.15s, 8.4s, 8.5vs, *9.05s, 9.2vs, 9.3vs*
$CH_3CH_2CH_2CH_2SCH_2COPh$[c,k]	6.8s, 6.9vs, 7.1s, 7.3s	7.6s, 7.65s, *7.85vs,* 8.1m, 8.35vs, 8.45s, *8.8s,* 9.1w, 9.3m 9.7w

Formula of compound	Characteristic absorption peaks,[a] μ: C-H deformation region
$C_6H_5SCH(OH)COPh$	*10.0s, 10.3vs,* 11.95 12.4s 13.3vs, 13.7m, 14.4vs, 14.6vs, 14.9m
$C_6H_5SCH(OAc)COPh$	9.95m, 10.4vs, 11.05s, 11.7m, 12.15m 13.1s, 13.15s, 13.25s 14.2m, 14.4vs, 14.6m
$C_6H_5SCH_2COPh$[c]	*9.85vs* 12.4w 13.4vs, 13.8s, 14.3s, 14.5s
$C_6H_5SOCH_2COPh$	*9.9vs, 10.0s* 12.4m 13.2vs, 13.4vs, 13.9vs, 14.5s, 14.7s
$C_6H_5SO_2CH_2COPh$[d]	*9.9s, 10.0s* 11.05m 12.1s, 12.95s, 13.25vs, 13.35vs 14.5s, 14.65s, 15.0m
$4\text{-}ClC_6H_4SCH(OH)COPh$[e]	*9.85m, 9.95m, 10.2vs* 11.95s, *12.25vs,* 12.45m, 13.3w, 13.7m, 13.9m, 14.15w, 14.55s, 14.85s
$4\text{-}ClC_6H_4SCH_2COPh$[c,f]	*9.95s, 10.05s* 12.2vs, 12.7m 13.35vs 14.55s
$4\text{-}ClC_6H_4SOCH_2COPh$[g]	*9.9vs, 10.0s* 12.1vs 13.2s, 13.4vs, 13.7s, 14.5vs
$CH_3SCH(OH)COPh$	*10.0m,* 10.2s, *10.35vs* *12.1vs,* 12.4s 13.55s, 14.2s, 14.6s, 14.95s
CH_3SCH_2COPh[c,h]	*9.8s, 9.95s,* 10.1s, 10.4s 12.1m, 12.4m, 13.2vs 13.7vs, 14.4vs 15.1m
$CH_3SO_2CH_2COPh$[i]	*9.9s* 10.3s, 10.35s 11.1s, 12.1w 13.0vs, 13.25s 14.0m, 14.5s, 15.7w
$CH_3CH_2SCH(OH)COPh$	*9.95m,* 10.05w, *10.2vs* *12.0vs,* 12.4m 13.5s 14.6vs, 14.9s
$CH_3CH_2SCH_2COPh$[c,j]	*9.9vs, 10.0s,* 10.1s, 10.35m 12.4s 13.4m, 13.7vs 14.6s, 15.1m
$CH_3CH_2CH_2CH_2SCH(OH)COPh$	*9.9m* *10.2vs* *12.0vs,* 12.4m 13.8s 14.65vs, 14.9s
$CH_3CH_2CH_2CH_2SCH_2COPh$[c,k]	*9.85vs, 9.95s,* 10.1m, 10.3i 12.4m 13.4s, 13.7s 14.6vs, 15.1m

[a] vs, very strong; m, medium; w, weak; i, inflection; in KBr pellets containing 5% of the compound examined. [b] In $CHCl_3$ solution. [c] Prepared by Wahl's method.[17] [d] Prepared by the method of Tröger and Beck[25]; m.p. 91–92°. [e] Prepared by method of Kipnis and Ornfelt[14]; m.p. 73–75°. *Anal.* Calcd. for $C_{14}H_{11}O_2SCl$: C, 60.32; H, 3.98; S, 11.20. Found: C, 60.51; H, 4.05; S, 11.00. [f] M.p. 79.5–80.5°; reported[22] m.p. 80°. [g] Prepared as described for phenylsulfinylacetophenone. [h] B.p. 100–105° (0.4 mm.); reported b.p. 131–132° (12 mm.). [i] M.p. 91–92°. [j] B.p. 98–101° (0.3 mm.); reported[21] b.p. 104–106° (0.3 mm.). [k] B.p. 107–110° (0.2 mm.); reported[24] b.p. 133° (2 mm.).

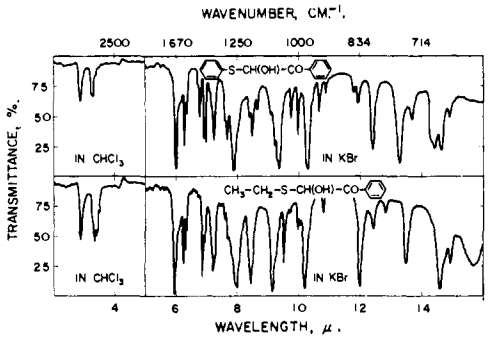

Fig. 1.—Infrared spectra of co-oxidation products of thiols and phenylacetylene.

A definite structure proof was obtained by a direct synthesis of these co-oxidation products Ia–Id. Hemimercaptals are known to be formed readily by the direct reaction of thiols and aldehydes.[13] Kipnis and Ornfelt[14] found that phenylglyoxal forms particularly stable hemimercaptals with a variety of thiols. However, they did not characterize their compounds beyond giving melting points and elemental analyses. We synthesized by their method the compounds which have been obtained by co-oxidation and characterized them by n.m.r. and infrared. Their spectra were identical with those of the corresponding co-oxidation products.

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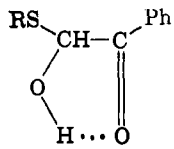
TABLE II

PARAMETERS OF NUCLEAR MAGNETIC RESONANCE SPECTRA OF CO-OXIDATION PRODUCTS OF THIOLS AND PHENYLACETYLENE; $RSO_xCH(Y)COPh$

			Chemical shifts of structural units, p.p.m. downfield from tetramethylsilane internal reference[a]			
R	x	Y	RSO_x	-CH	(Y)-	CoPh
Phenyl[c]	0	OH	m7.2–7.7, m7.8–8.1	s6.32	s4.47	m7.2–7.7, m7.8–8.1
	0	OAc				
	0	H	m7.2–7.7, m7.8–8.1	s4.15		m7.2–7.7, m7.8–8.1
	1	H	m7.2–8.0	q4.44[b]		m7.2–8.0
	2	H	m7.1–8.0	s4.73		m7.1–8.0
4-Chlorophenyl[c]	0	OH	s7.25	s6.25	s4.63	m7.3–7.7, m7.9–8.2
	0	H	m7.1–8.0	s4.20		m7.1–8.0
	1	H	m7.2–7.8	q4.32[b]		m7.2–7.8
Methyl	0	OH	s1.97	s6.15	s4.53	m7.3–7.7, m7.9–8.2
	0	H	s2.08	s3.73		m7.2–7.7, m7.8–8.2
	2	H	s3.12	s4.62		m7.2–7.6, m7.8–8.1
Ethyl	0	OH	t1.20 m2.62[f]	s6.20	s4.58	m7.3–7.7, m7.9–8.2
	0	H	t1.25 m2.58	s3.78		m7.2–7.6, m7.8–8.2
n-Butyl	0	OH	t0.84,[d] m1.42, t2.6[f]	s6.22	s4.60	m7.3–7.7, m7.7–8.2
		H	t0.84,[d] m1.45, t2.53[e]	s3.75		m7.3–7.7, m7.8–8.1

[a] s, singlet; t, triplet; q, quartet; m, multiplet. In the case of solid compounds, deuteriochloroform was used as a solvent. [b] AB type quartet, J = 14 c.s.p., δ = 0.26 p.p.m. [c] N.m.r. signals of R and Ph cannot usually be distinguished. [d] J = 7 c.p.s. [e] J = 7.5 c.p.s. [f] High order multiplicity due to asymmetric hemimercaptal carbon atom.

In their infrared spectra all the hemithioacetals show a strong OH-stretching absorption at 2.9μ[15a] and a strong C=O absorption[15b] band at about 6 μ (Table I, Fig. 1). The OH-band is sharp both in a $CHCl_3$ solution and in a KBr pellet. Upon dilution from 1 molar to 0.01 molar $CHCl_3$ solution it varied only very slightly in wave length (2.91 instead of 2.9 μ). Such behavior is characteristic of single bridged intramolecular hydrogen bonding of alcohols.[15a,16] Therefore, the following structure for the phenylglyoxal hemithioacetals is proposed.



The n.m.r. spectra of the phenylglyoxal hemithioacetals showed the expected multiplets in the aromatic region and the signals of the substituent of the hemithioacetal group. In addition, there were two other signals of one proton intensity each. On the basis of their chemical shifts and mutual splitting into doublets, they can be assigned to the protons on the α-carbon and the hydroxyl group, respectively. This splitting occurs only in fresh solutions of the pure compounds and is a result of H–C–O–H spin coupling under conditions of slow proton exchange.[17] On standing or on the addition of aqueous hydrochloric acid, these doublets collapse into singlets owing to the increase of the rate of proton exchange (Table II, Fig. 2). In alkylthiohemiacetals the methylene group next to the sulfur atom showed a high order of multiplicity (Table II, Fig. 2). This is probably due to interaction of the proton at the asymmetric acetal carbon through the sulfur atom.[18]

It was reported recently by Schroeder and Dodson[19] that some heterocyclic β-ketosulfoxides rearrange readily to the corresponding hemithioacetals. Such reduction reactions of four-valent sulfoxide sulfur with concurrent oxidation of the α-carbon occur frequently.

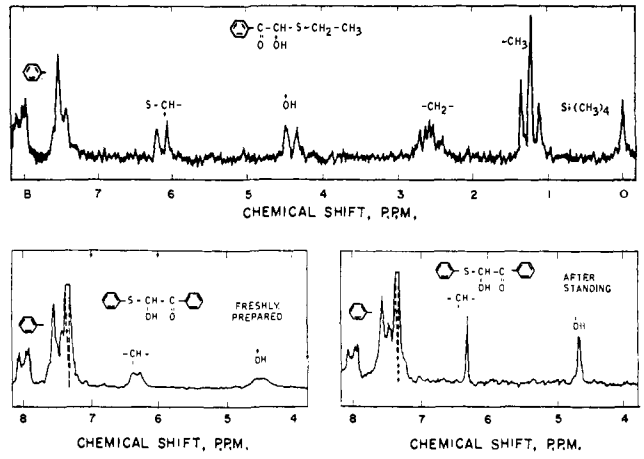


Fig. 2.—N.m.r. spectra of phenylglyoxal hemimercaptals.

Thus, acetylation of simple sulfoxides with acetic anhydrides yields hemithioacetal acetates,[20] chlorination of sulfoxides by thionyl chloride gives α-chlorosulfides,[21] and reactions of sulfides with peracid anhydrides,[22] esters[23] and chlorides[24] yield hemithioacetal acetates, probably through sulfenium salts.

It was, therefore, of interest to determine whether the β-ketosulfoxides II that are isomeric with our co-oxidation products would also undergo a similar rearrangement to form I. Such a reaction would offer additional support for the assumed structures and some information with regard to the possible course of the co-oxidation reaction. The required ω-alkyl- and ω-arylsulfinylacetophenones (II) should be available through the oxidation of the corresponding ω-mercaptoacetophenones.[25–32] Therefore, phenyl-, methyl-, ethyl- and butyl-mercaptoacetophenone were synthesized from ω-bromoacetophenone and the corresponding sodium

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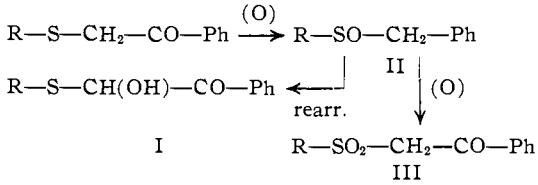
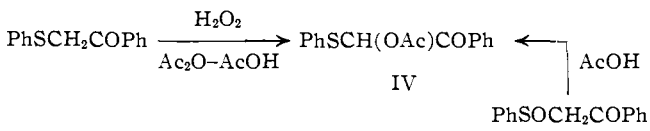
(32) L. M. Long, *J. Am. Chem. Soc.*, **68**, 2159 (1946).

mercaptides. Their oxidation with hydrogen peroxide–acetic acid can yield the products I–III



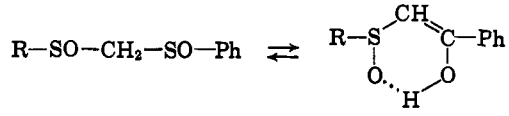
When equimolar amounts of ω-phenylmercaptoacetophenone and hydrogen peroxide were allowed to react in acetic acid solution, the known ω-phenylsulfinylacetophenone[25] (II, R = Ph), isomeric with the corresponding phenylglyoxal hemithioacetal (I), was obtained. When this oxidation was carried out at higher temperatures and in the presence of acetic anhydride, the rearranged product, ω-phenylmercapto-(acetoxy)-acetophenone (IV), was obtained. This compound has been previously prepared by refluxing phenylsulfinylacetophenone in acetic acid.[33]



Oxidation of the ω-alkylmercaptoacetophenones by hydrogen peroxide–acetic acid at 60°, on the other hand, yielded no sulfoxides but only phenylglyoxal hemithioacetals. These were identical with the corresponding co-oxidation products and the products of the direct synthesis.

For comparative studies of their infrared and n.m.r. spectra, we have also synthesized some substituted ω-sulfonylacetophenones[34,35] by the reaction of sodium benzenesulfinate with ω-bromoacetophenone.[36,37]

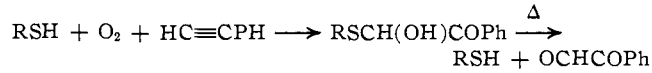
Since it was reported that sulfoxides form intermolecular hydrogen bonds with alcohols,[38] it was thought that ω-sulfinylacetophenones may exist in the enol form due to stabilization by a sterically favored 6-membered intramolecular hydrogen bonding.[39]



The complete absence of OH stretching absorption around 3 μ (Table I) indicates, however, the lack of any enolization. It was, therefore, concluded that even a very favorable and likely case of hydrogen bonding will not cause a tautomerization of substituted sulfinylacetophenones. The same was found to be true for the substituted mercapto- and sulfonylacetophenones (Table I).

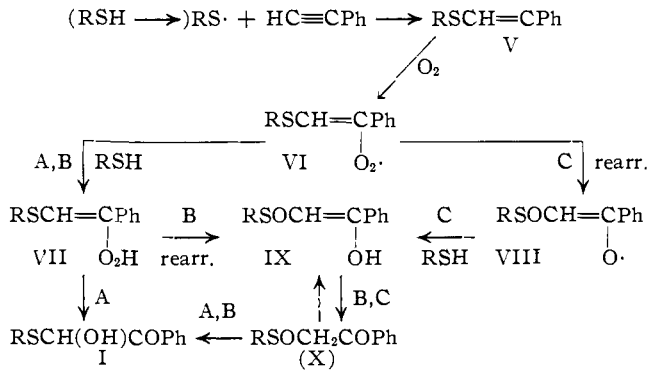
Discussion

The co-oxidation of thiols and phenylacetylene represents a new type of selective oxidation of the acetylene bond. In the case of phenylacetylene, the reaction leads to phenylglyoxal hemithioacetals as the first stable products. These, in turn, can be readily cleaved by simple vacuum distillation to yield monomeric phenylglyoxal with the regeneration of the thiol



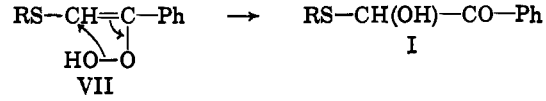
The described co-oxidation reactions are free radical reactions with a chain mechanism. This is indicated by the marked increase of the rate of reaction under ultraviolet irradiation.

The formation of the phenylglyoxal hemithioacetal end-products can be rationalized by assuming one or more of the three reaction paths A, B and C



It seems sound to assume that the chain is started by the addition of a mercapto radical to the end carbon of phenylacetylene to form a highly reactive vinylic radical. This is also the first step in the free radical addition of thiols to acetylenes.[40] In the co-oxidation reaction, the vinylic radical intermediate V combines with molecular oxygen to form the vinylperoxy radical VI. This can either abstract a hydrogen from thiol to yield a vinylic hydroperoxide (VII) or rearrange to form a vinyloxy radical (VIII). Both of these intermediates might rearrange to the same ω-alkyl- or ω-arylsulfinylacetophenone X. On further rearrangement, the ω-sulfinyl acetophenones would yield the hemithioacetal end-products I.

According to the most likely short reaction route A, the vinylic hydroperoxide intermediate VII yields the end-product I in the one-step rearrangement[41]



The formation of a sulfinylacetophenone by the hydroperoxide route B and/or the vinyloxy radical route C is analogous to the mechanisms proposed by Kharasch for the synthesis of sulfinylethanols on the co-oxidation of monoölefins and thiols.[3] In the monoolefin–thiol co-oxidation reaction, the hydroperoxide route (B) has been established by the actual isolation of these intermediates, which was reported earlier in this series.[4] The formation of a hydroperoxide intermediate VII (R = Ph) is also indicated in the co-oxida-

(33) W. J. Kenney, J. A. Walsh and D. A. Davenport, *J. Am. Chem. Soc.*, **83**, 4019(1961).

(34) W. E. Truce and R. H. Knospe, *ibid.*, **77**, 5063 (1955).

(35) L. Field, J. E. Lawson and J. W. McFarland, *ibid.*, **78**, 4389 (1956); L. Field and J. W. McFarland, *ibid.*, **75**, 5582 (1953).

(36) J. Tröger and O. Beck, *J. prakt. Chem.*, **287**, 289 (1913).

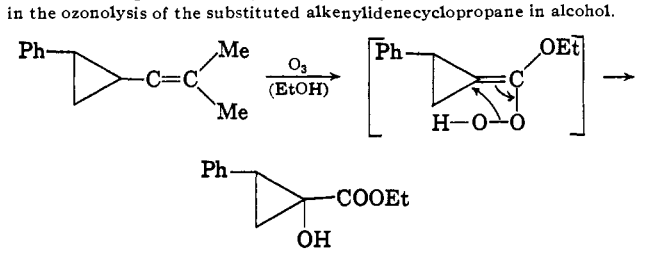
(37) L. Field, *J. Am. Chem. Soc.*, **74**, 3919 (1952).

(38) D. Barnard, J. M. Fabian and H. P. Koch, *J. Chem. Soc.*, 2442 (1949).

(39) E. H. Holst and W. C. Cornelius, *J. Org. Chem.*, **23**, 1881 (1958).

(40) A. A. Oswald and K. Griesbaum, Chapter on Radical Additions of Thiols to Diolefins and Acetylenes, in "Organic Sulfur Compounds," edited by N. Kharasch, Pergamon Press, New York, N. Y., in press.

(41) A similar type of mechanism has been suggested recently by Hartzler for the rearrangement of a hypothetical vinylic hydroperoxide intermediate in the ozonolysis of the substituted alkenylidenecyclopropane in alcohol.



H. D. Hartzler, *J. Am. Chem. Soc.*, **83**, 4991 (1961).

tion of benzenethiol and phenylacetylene. This excludes the vinyloxy radical route C. Moreover, the subsequent rearrangement of the hydroperoxide VII to ω-phenylsulfinylacetophenone (X, R = Ph) is unlikely, since the latter would not rearrange to form a hemithioacetal under the conditions of the co-oxidation. This indicates that the co-oxidation of benzenethiol and phenylacetylene proceeds *via* the direct route, A.

In the co-oxidation of aliphatic thiols and phenylacetylene, however, it is impossible to decide which is the preferred reaction path. Route B may represent it in this case since we have found that the oxidation of alkylmercaptoacetophenones yielded hemithioacetals. In that case the intermediate ω-alkylsulfinylacetophenones rearranged spontaneously.

Recent work[42] on the mechanism of the rearrangement of phenylsulfinylacetic acid indicates that it takes place intramolecularly. A similar intramolecular mechanism may also operate in the oxidation–reduction reactions of our hydroperoxide intermediates.

It can be concluded therefore that ω-alkylsulfinylacetophenones are possible intermediates in the co-oxidation of aliphatic thiols. However, even in this case, the rearrangement of the hydroperoxide through the sulfinylacetophenone (route B) is not more probable than the direct rearrangement to the end-product (route A), since no sulfinylacetophenone intermediate could ever be isolated.

Experimental

Materials.—Phenylacetylene from Eastman Kodak Co. was redistilled before use. The oxygen was of 99.6% purity. The thiols were C.P. chemicals.

Methods and Equipment.—The oxygenations were carried out at atmospheric pressure in a 4-necked round-bottom flask, equipped with a dewar condenser, a thermometer, a sintered glass inductor with 7.5 cm.^{2} sintered area, a magnetic stirrer and, in the case of aromatic thiol–phenylacetylene co-oxidation, a dropping funnel. After an initial purging, the oxygenation rate was adjusted so that about one bubble of gas left the reaction mixture per second.

Methods of Analysis.—Carbon and hydrogen were analyzed by the micro-combustion technique. Sulfur analyses were made using the Parr bomb method.

Hydroperoxide contents were determined on the basis of the sodium iodide oxidized in cold acetic acid solution. The nuclear magnetic resonance spectra were recorded with a Varian model A-60 proton resonance spectrometer. The infrared spectra were obtained on a Baird recording spectrophotometer, model B. The hydrogen bonding studies were made using a CaF_2 prism. Liquid–gas chromatography was carried out on a Perkin–Elmer model 226 temperature programmed gas chromatograph using a 200-ft. phenylsilicone–nitrilesilicone coated column.

Co-oxidation of Benzenethiol and Phenylacetylene at Low Temperature.—A solution of 7.7 g. (0.075 mole) of phenylacetylene in 640 ml. of *n*-pentane was purged with oxygen at 75°. The reaction flask was connected to a 2-l. gas buret filled with oxygen. Dropwise addition of 8.2 g. (0.07 mole) of benzenethiol to the stirred solution was started. After an induction period of about 5 minutes, a rapid absorption of oxygen began. From that time on the rate of thiol addition was adjusted from time to time to the rate of oxygen absorption. The solution soon turned yellow, and within a few minutes a solid precipitate began to form. The thiol addition was completed in an hour. The reaction mixture was stirred for an additional 20 minutes in an oxygen atmosphere until the theoretical amount of oxygen was absorbed. Then the oxygen was removed from the mixture by bubbling nitrogen through it.

Half of the mixture was filtered and dried cold to yield 7 g. (76.5%) of a slightly yellow unstable solid that melted at about −8°. This solid was analyzed immediately. It showed a positive hydroperoxide test. On standing for 24 hr. at −10°, just below its initial melting point, the primary product lost its peroxide content. It no longer melted below room temperature. Its infrared spectrum was identical with the hemithioacetal obtained by direct synthesis from benzenethiol and phenylglyoxal. The m.p. was 93–94° after recrystallization from acetic acid. Kipnis and Ornfelt[14] reported m.p 97–98°.

The other half of the reaction mixture was kept under nitrogen atmosphere, allowed to come to −10°, and kept there for 2 days. During this period a rearrangement of the primary product occurred. The solid did not melt on coming to room temperature. It was filtered at room temperature to yield 5.5 g. (60%) of the hemithioacetal Id.

The Co-oxidation of Benzenethiol and Phenylacetylene at 0°.—An ice–water-cooled solution of 7.7 g. (0.07 mole) of phenylacetylene in 600 ml. of *n*-heptane was treated with 8.2 g. (0.075 mole) of benzenethiol in an oxygen atmosphere in a manner described above. After 1 minute the originally colorless solution became hazy and turned yellow. The thiophenol was added within 30 minutes. During this time, the rate of oxygen absorption was between 50 and 80 ml./minute and the temperature of the mixture rose from 3° to 10°. After all of the thiol had been added, the oxygen uptake ceased within 10 minutes and the temperature dropped to 6°. The total volume of oxygen absorbed was 1710 ml. (calculated for standard conditions), 102% of the theoretical amount required. The heptane was removed from the reaction mixture by vacuum distillation. The remaining semisolid material yielded 4.3 g. (23.5%) of the crystalline hemithioacetal.

The mother liquor contained about 3.5 g. (45.5%) of unconverted phenylacetylene and 1.5 g. of a high boiling yellow liquid. The latter consisted of six components in almost equal amounts as shown by gas chromatography.

Co-oxidation of Methanethiol and Phenylacetylene at Low Temperature.—A mixture of 10.2 g. (0.1 mole) of phenylacetylene and 900 ml. of pentane in a 1-l. quartz flask was purged with oxygen for 1 minute at −70°. Then 5.3 g. (0.11 mole) of methanethiol was added at once and the oxygen flow was adjusted as mentioned above. The mixture was irradiated with a 100 w. hign pressure Hanovia ultraviolet lamp. The temperature was kept below −60°. The mixture became slightly yellow soon after the start of the reaction. The solid reaction product began to precipitate after 1 hour. After a conversion of 70% was reached in 20 hours, the mixture was worked up. The slightly yellow solid was filtered to yield 11 g. (86%) of the hemithioacetal Ib, m.p. 99–101°.

Anal. Calcd. for $C_9H_{10}O_2S$: S, 59.31; H, 5.53; S, 17.59. Found: C, 59.41; H, 5.29; S, 17.18.

The Co-oxidation of Methane- and Ethanethiol and Phenylacetylene at 0°.—The co-oxidation reaction was carried out the same way as described in the previous experiment. However, the yields of the hemithioacetals were much lower, 36 and 43%, respectively.

Phenylglyoxal ethylhemithioacetal was previously synthesized from phenylglyoxal and ethanethiol by Kipnis and Ornfelt.[14] They reported m.p. 78–80°. Our compound from the co-oxidation and from the direct synthesis had a m.p. of 75–76°. The co-oxidation product had the expected elemental composition.

Anal. Calcd. for $C_{10}H_{12}O_2S$: C, 61.19; H, 6.16; S, 16.34. Found: C, 61.09; H, 6.16; S, 16.15.

The co-oxidation of butanethiol and phenylacetylene is a very slow reaction even under ultraviolet irradiation. In 3.5 days at room temperature only 70% of the thiol was converted. The corresponding hemithioacetal was isolated in a 34% yield. Its melting point after recrystallization from *n*-heptane is 56–57.5°.

Anal. Calcd. for $C_{12}H_{16}O_2S$: C, 64.25; H, 7.18; S, 14.29. Found: C, 64.30; H, 7.34; S, 14.18.

Oxidation of ω-Alkylmercaptoacetophenones.—To an ice-cooled mixture of 0.024 mole of the ω-alkylmercaptoacetophenone in 25 ml. of acetic acid, 2.9 g. of 30% aqueous H_2O_2 was added dropwise below 40°. After the initial reaction was over, the mixture was kept at 60° for 4 hours and then left standing at room temperature for 3 days. On dilution with water, a separate layer of a yellow, viscous liquid was formed. It was dissolved in ether and dried over Na_2SO_4. When the ether was removed by vacuum distillation, the remaining yellow oil crystallized spontaneously, on addition of a few drops of *n*-pentane at low temperature. The solid was recrystallized from *n*-pentane.

ω-Phenylmercapto-(acetoxy)-acetophenone.—To 11.4 g. (0.05 mole) of ω-phenylmercaptoacetophenone in a mixture of 40 ml. of acetic anhydride and 20 ml. of acetic acid, 5.7 g. of 30% H_2O_2 was added. The mixture came, for a short while, to reflux temperature. Then it was left standing at room temperature for 5 days. On adding water, the ω-phenylmercapto-(acetoxy)-acetophenone precipitated immediately. It was filtered off and recrystallized from *n*-heptane to form white needles, m.p. 67–68°.

Its infrared spectrum shows two strong bands at 4.7 and 5.9 μ which can be assigned to the C=O stretching vibrations of acetyl and benzoyl groups, respectively (Table I). These assignments are supported by comparison with the infrared spectrum of the 2,4-dinitrophenylhydrazone of the compound. The latter showed only the 4.7 μ bond. The n.m.r. spectrum also supports the assigned structure.

ω-Phenylsulfinylacetophenone.—To a solution of 12.2 g. (0.05 mole) of ω-phenylmercaptoacetophenone in 50 ml. of acetic acid, 5.67 g. (0.05 mole) of 30% aqueous hydrogen peroxide was added

(42) D. Walker and J. Leib, *Can. J. Chem.*, **40**, 1242 (1962).

dropwise with stirring at room temperature. To complete the reaction, the mixture was allowed to stand overnight. Then it was diluted with 300 ml. of water; the precipitated heavy oil was washed with 100 ml. of a 4% aqueous sodium hydroxide solution and dissolved in a minimum amount of hot benzene–heptane mixture. From the solution 6.5 g. (53%) of phenylsulfinylacetophenone, m.p. 79–80°, crystallized on standing at room temperature.

Acknowledgment.—The authors wish to acknowledge helpful discussions with Professor G. A. Russell and Dr. P. V. Smith, Jr. They also wish to thank A. M. Palmer and T. J. Jermansen for valuable technical help, and D. E. Bachert for recording the infrared spectra.

[CONTRIBUTION FROM THE RESEARCH DIVISION, POLAROID CORPORATION, CAMBRIDGE 39, MASS.]

Spectral Shifts in Anthraquinone Dyes Caused by Non-conjugated Substituents

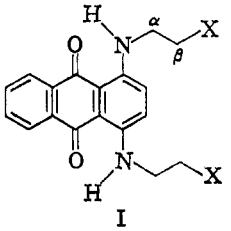
BY MYRON S. SIMON

RECEIVED JANUARY 30, 1963

Anomalous absorption spectra in the 400–700 mμ region caused by β-amino groups on the alkyl chains of 1,4-bis(N-alkylamino)-anthraquinone dyes are reported and discussed.

In a study of N-alkylated 1,4-diaminoanthraquinones an interesting anomaly was observed in the visible spectra of β-amino ethyl substituted derivatives. The normal absorption spectra of 1,4-bis(N-alkylamino)-anthraquinones show peaks close to 642 and 595 mμ and an inflection around 555 mμ in 2-methoxyethanol, benzene or hexane. The data for 1,4-bis-(isopropylamino)-anthraquinone (m.p. 179–180°) or 1,4-bis-(*sec*-butylamino)-anthraquinone (m.p. 155–158°) are typical, and correspond to type I of Fig. 1. The position of these peaks and over-all shape of the absorption envelope is unchanged by substituting hydroxyl groups for a β-hydrogen on the N-alkyl substituents. 1,4-Bis-(β-hydroxyethylamino)-anthraquinone (I, X = OH; m.p. 242.5–244°) has a spectrum identical with those cited above.

Replacement of a β-hydrogen by an amino group leads to a marked change in the visible absorption spectrum.



I

The peaks are shifted to shorter wave length, but peak height is not altered, and a new, broad absorption band of relatively low intensity appears in the 400–500 mμ region. The curve of 1,4-bis-(β-aminoethylamino)-anthraquinone (I, X = NH_2; m.p. 207–208°) dissolved in 2-methoxyethanol is shown in Fig. 1 and is labeled a type II spectrum for easy reference. The new peak (435 mμ, ε 4500, $MeOCH_2CH_2OH$) is shifted in less polar solvents to lower wave length (419 mμ, 4400, benzene; 405 mμ, 4800, hexane), while the high intensity bands are shifted in the opposite direction (605 mμ, ε 21400; 563 mμ, ε 16800, $CH_3OCH_2CH_2OH$; 616 mμ, ε 21400; 571 mμ, ε 17000, benzene; 613 mμ, ε 21400; 568 mμ, ε 17800, hexane) (I, X = NHC_2H_5). Spectral data are summarized in Table I.

In an effort to explain this phenomenon a number of related compounds were synthesized: (1) It was found that the bridge of two carbon atoms between the nitrogens of the side chain is essential for the spectral shift: 1,4-bis(γ-aminopropylamino)-anthraquinone (m.p. 135.5–137°) and similar dyes with a longer bridge between nitrogens of the side chain have the type I curve of the model compounds.

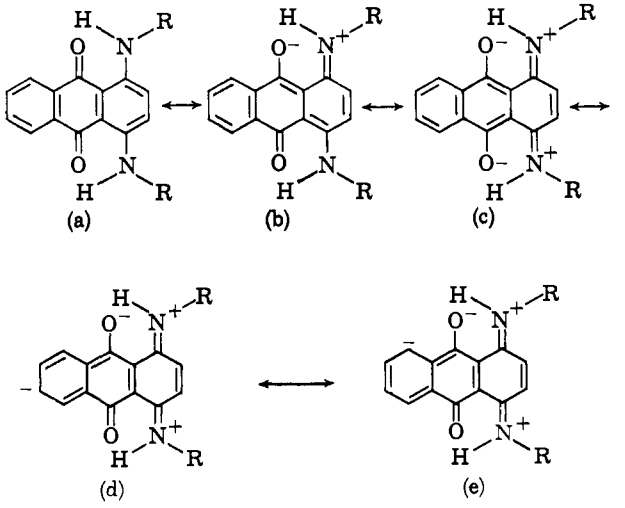
(2) Substitution of one hydrogen atom on the β-amino group by an alkyl group does not cause this phenomenon to disappear: 1,4-bis-(β-N-ethylamino ethylamino)-anthraquinone (I, X = NHC_2H_5; m.p 120.5–122°) has the type II spectrum.

(3) At least one hydrogen on the β-amino group is necessary: 1,4-bis-(β-N-diethylaminoethylamino)-anthraquinone (m.p. 112–112.5°) has a spectrum identical with that shown by compounds of type I.

(4) Basicity of the β-nitrogen is a requirement for appearance of the type II spectrum: 1,4-bis-(β-acetamidoethylamino)anthraquinone (m.p. 218–219°) has a normal, type I, spectrum.

(5) This phenomenon appears to be limited to the 1,4-diamino series: 1,5-bis-(β-aminoethylamino)-anthraquinone (m.p. 195–199° dec.) has the same spectrum as simpler 1,5-bis-(alkylamino)-anthraquinones while 5,8-dihydroxy-1,4-bis-(β-aminoethylamino)-anthraquinones are shifted in the same manner as the simpler 1,4-diamino series described above, and have a type II spectrum with maxima at 642, 591, ~549 and 443 mμ (2-methoxyethanol).

The 1,4-diaminoanthraquinone absorption system appears to have unique properties which are imperfectly understood. A detailed discussion of the problem may be found in the papers of Egerton and Roach[1] and Peters and Sumner,[2] which refer to earlier work. Thus, while the 1,5-diaminoanthraquinone chromophore seems to be the arithmetical sum of two 1-aminoanthraquinone chromophores,[3] the 1,4-system exhibits a more complicated spectrum which has not been related in a



(a) (b) (c) (d) (e)

(1) G. S. Egerton and A. G. Roach, *J. Soc. Dyers and Colourists*, **74**, 405 (1958).

(2) R. H. Peters and H. H. Sumner, *J. Chem. Soc.*, 2101 (1953).

(3) C. J. P. Spruitt, *Rec. trav. chim.*, **68**, 329 (1949).