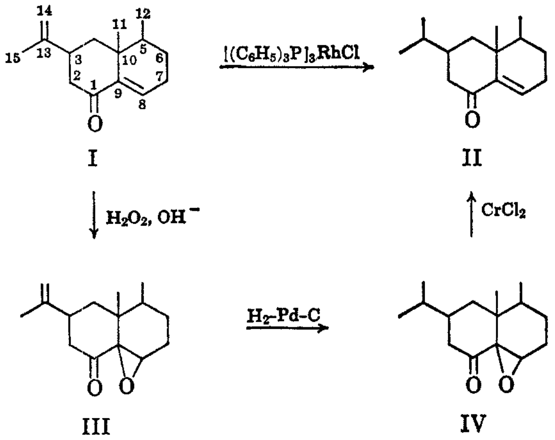
(II). Attempted selective hydrogenation of eremophilone (I) with palladium on a variety of supports and in various solvents all led to the same result, namely, more rapid reduction of the conjugated double bond.

Bromination and dehydrobromination of tetrahydroeremophilone gave mixtures of compounds. Reduction of eremophilone (I) with diborane was also attempted, but again without success. The three-step procedure (I → III → IV → II) was then devised and found to proceed satisfactorily in 63% over-all yield (see Scheme I).

SCHEME I



Subsequently, we tried direct reduction of eremophilone using the new, homogenous hydrogenation catalyst, tris(triphenylphosphine)chlororhodium(I).[1] The hydrogenation proceeded very well using this catalyst and in this manner dihydroeremophilone was obtained in 94% yield. We have also looked at the reduction of other compounds, and in general we find that a terminal double bond can be selectively reduced in the presence of other more substituted double bonds.[2,3]

Experimental Section

Melting points were determined on a Kofler micro hot stage and are corrected. The infrared spectra were determined on a Perkin-Elmer Infracord, Model 137, and nmr spectra were obtained with a Varian A-60 spectrometer on solutions in carbon tetrachloride.

Eremophilone oxide (III) was prepared by the published procedure[4] in 78% yield: mp 60–61° (lit.[1] mp 63–64°); $\lambda_{\max}^{\mathrm{CHCl_3}}$ 5.82, 11.18 μ; nmr δ 2.83 m (epoxy-ring hydrogen), 4.75 ($>C{=}CH_2$).

Dihydroeremophilone Oxide (IV).—A solution of 2.16 g of eremophilone oxide (III) was hydrogenated over 0.050 g of 5% palladium on carbon. Removal of the catalyst and evaporation of the solvent afforded the product 2.08 g (95% yield): mp 50–51° (lit.[1] mp 53–54°), $\lambda_{\max}^{\mathrm{CHCl_3}}$ 5.82 μ, nmr δ 2.80 m (epoxy-ring hydrogen).

13,14-Dihydroeremophilone (II).—A solution of 2.0 g of dihydroeremophilone oxide (III) in 40 ml of acetic acid was stirred at room temperature under nitrogen while 60 ml of 0.5 *M* chromous chloride[5] was added. After stirring for 2.5 hr the solution was then poured into water and isolated in the usual manner by extraction with methylene chloride. Distillation afforded 1.65 g (85% yield) of dihydroeremophilone (II): bp 100° (1 mm); $n^{25}\mathrm{D}$ 1.5015; $[\alpha]\mathrm{D}$ −175° (*c* 0.411, methanol); $\lambda_{\max}^{\mathrm{film}}$ 5.92 μ (conjugated C=O), 6.16 (conjugated C=C); $\lambda_{\max}^{\mathrm{EtOH}}$ 242 mμ (ϵ 6500); mass spectrum *m/e* 220 (M^+), 205, 178 (base peak), 153, 149, 135, 121, 109, 107.

Anal. Calcd for $C_{15}H_{24}O$: C, 81.76; H, 10.98. Found: C, 81.69; H, 11.08.

Dihydroeremophilone (II) by Direct Reduction.—A solution of 0.102 g of eremophilone and 0.070 g of tris(triphenylphosphine)-chlororhodium(I)[6] in 15 ml of benzene was stirred under an atmosphere of hydrogen for 8 hr. The solution was then passed through an alumina column (3 g), which, on evaporation of the solvent and distillation, afforded 0.097 g (94% yield) of pure 13,14-dihydroeremophilone (II).

Registry No.—II, 10316-33-3; III, 10316-34-4; IV, 10316-35-5.

Acknowledgment.—The authors appreciate greatly support by a grant from the Eli Lilly Foundation.

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[1] J. F. Young, J. A. Osborn, F. H. Jardine, and G. Wilkinson, *Chem. Comm.*, **131** (1965).

[2] M. Brown, unpublished results.

[3] For other reductions using this catalyst, see C. Djerassi and J. Gutzwiller, *J. Am. Chem. Soc.*, **88**, 4538 (1966); A. J. Birch and K. A. M. Walker, *Tetrahedron Letters*, 4939 (1966).

[4] A. E. Bradfield, A. R. Penfold, and J. L. Simonsen, *J. Chem. Soc.*, 2749 (1932). The eremophilone was isolated from the wood oil of *Eremophilia mitchelli*. The oil was kindly supplied by the Museum of Applied Arts and Sciences, Sydney, Australia.

[5] G. Rosenkranz, O. Mancera, J. Gatica, and C. Djerassi, *J. Am. Chem. Soc.*, **72**, 4077 (1950).

Preparation of Alkoxysulfonium Salts by Oxidation of Sulfides with Positive Halogen Compounds[1,2a]

CARL R. JOHNSON[2b] AND MICHAEL P. JONES

Department of Chemistry, Wayne State University,
Detroit, Michigan 48202

Received December 27, 1966

The first and most widely investigated method of preparation of alkoxysulfonium salts consists of O alkylation of the respective sulfoxides (synthesis of the oxygen–carbon bond).[3] Synthesis of the sulfur–oxygen bond, on the other hand, has received little attention. Only the reaction of dimethylchlorosulfonium salts with ethanol, propyl alcohol, and isopropyl alcohol to give the respective alkoxysulfonium salts have been reported.[4] However, *t*-butoxysulfonium chlorides have been postulated as unstable intermediates in the oxidation of sulfides to sulfoxides with *t*-butyl hypochlorite.[5]

The obvious convenience of a method for the preparation of alkoxysulfonium salts directly from sulfides prompted an investigation of the alkyl hypochlorite and related oxidations of sulfides in an attempt to isolate and characterize the intermediate salt.[6]

A variety of sulfides was oxidized with equimolar amounts of either *t*-butyl or isopropyl hypochlorite in methylene chloride at −78°. The initial alkoxysul-

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[1] (a) Part VI in the series, Chemistry of Sulfoxides. (b) Part V: C. R. Johnson and D. McCants, Jr., *J. Am. Chem. Soc.*, **87**, 5404 (1965).

[2] (a) We gratefully acknowledge support by the National Science Foundation (Grant No. GP-5944); (b) Alfred P. Sloan Research Fellow, 1965–1968.

[3] H. Meerwein, E. Battenberg, H. Gold, E. Pfeil, and G. Willfang, *J. Prakt. Chem.*, **154**, 83 (1939); S. G. Smith and S. Winstein, *Tetrahedron*, **3**, 317 (1958); S. Kabuss, *Angew. Chem., Intern. Ed. Engl.*, **5**, 675 (1966).

[4] H. Meerwein, K. Zenner, and R. Gipp, *Ann.*, **688**, 67 (1965).

[5] P. Skell and M. F. Epstein, 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April 1964, Abstracts, p 26N.

[6] In a recent communication, K. Torssell [*Tetrahedron Letters*, 4445 (1966)] has indicated that "In connection with work on positive halogen compounds new routes to alkoxydimethylsulfonium salts were developed." No additional details were given.

TABLE I

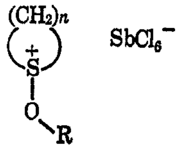
ALKOXYSULFONIUM HEXACHLOROANTIMONATES

Sulfide	Hypochlorite	Yield, %	Mp, °C	Formula	Calcd, % C	Calcd, % H	Found, %[a] C	Found, %[a] H
Tetramethylene	*t*-Butyl	71.6	86–87.5	$C_8H_{17}Cl_6OSSb$	19.38	3.46	19.62	3.53
Pentamethylene	*t*-Butyl	72.3[b]	109–111	$C_9H_{19}Cl_6OSSb$	21.21	3.76	21.29	3.88
Hexamethylene	*t*-Butyl	71.2[b]	80–81	$C_{10}H_{21}Cl_6OSSb$	22.93	4.04	23.01	4.16
Isopropyl	*t*-Butyl	81.7[c]	83–84	$C_{10}H_{23}Cl_6OSSb$	22.84	4.41	23.09	4.33
Phenyl	*t*-Butyl	76.1[c]	124–126	$C_{16}H_{19}Cl_6OSSb$	32.36	3.23	31.97	3.02
p-Chlorothioanisole	*t*-Butyl	34.9	65–66	$C_{11}H_{16}Cl_7OSSb$	23.33	2.85	23.20	2.86
t-Butyl	*t*-Butyl	*d*						
Trimethylene	*t*-Butyl	*d*						
Tetramethylene	Isopropyl	28.4[b,c]	125.5–127.5	$C_7H_{15}Cl_6OSSb$	17.45	3.14	17.52	3.15
Pentamethylene	Isopropyl	23.1	143–144	$C_8H_{17}Cl_6OSSb$	19.38	3.46	19.18	3.34
Hexamethylene	Isopropyl	30.9[b]	139–141	$C_9H_{19}Cl_6OSSb$	21.21	3.76	20.92	3.78
Isopropyl	Isopropyl	66.0	165–167	$C_9H_{21}Cl_6OSSb$	21.12	4.14	21.19	4.08
Phenyl	Isopropyl	33.7[b,c]	120.5–121.5	$C_{15}H_{17}Cl_6OSSb$	31.07	2.96	31.20	3.10
p-Chlorothioanisole	Isopropyl	29.6[b,e]	100–102	$C_{10}H_{14}Cl_7OSSb$	21.75	2.56	21.73	2.66
t-Butyl	Isopropyl	*d*						
Trimethylene	Isopropyl	*d*						

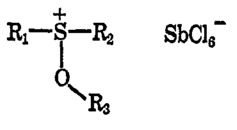
[a] Analyses by Midwest Microlabs, Inc., Indianapolis, Ind. [b] Yield after several recrystallizations. [c] Decomposed while drying in vacuum desiccator; stable indefinitely if stored immediately in refrigerator. [d] Decomposed before data could be obtained. [e] Formed initially as an oil.

TABLE II

NMR SPECTRA[a]



I

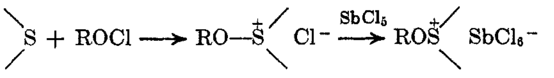


II

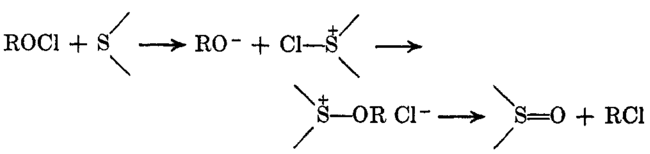
Compd	Chemical shift, ppm OCH	OCCH$_3$	SCH	SCCH and SC$_2$CH	Aromatic
Ia, R = *t*-C_4H_9; *n* = 4	...	1.59 s	3.58 m	2.50 m	...
Ib, R = *t*-C_4H_9; *n* = 5	...	1.60 s	3.46 m	1.96 m	...
Ic, R = *t*-C_4H_9; *n* = 6	...	1.59 s	3.57 m	2.00 m	...
IIa, R_1 = R_2 = *i*-C_3H_7; R_3 = *t*-C_4H_9	...	1.60 s	3.66 m	1.59 d	...
IIb, R_1 = R_2 = C_6H_5; R_3 = *t*-C_4H_9	...	1.60 s	...	...	7.77 m
IIc, R_1 = *p*-ClC_6H_4; R_2 = CH_3; R_3 = *t*-C_4H_9	...	1.60 s	3.35 s	...	7.86 q
Id, R = *i*-C_3H_7; *n* = 4	4.83 h	1.52 d	3.70 m	2.51 m	...
Ie, R = *i*-C_3H_7; *n* = 5	4.84 h	1.56 d	3.52 m	2.06 m	...
If, R = *i*-C_3H_7; *n* = 6	4.85 h	1.52 d	3.73 m	2.01 m	...
IId, R_1 = R_2 = R_3 = *i*-C_3H_7	4.72 h	1.56 d	3.81 h	1.58 d	...
IIe, R_1 = R_2 = C_6H_5; R_3 = *i*-C_3H_7	5.16 h	1.54 d	...	...	7.87 m
IIf, R_1 = *p*-ClC_6H_4; R_2 = CH_3; R_3 = *i*-C_3H_7	4.89 h	1.56 d, 1.46 d	3.57 s	...	7.93 q

[a] Spectra were obtained in sulfur dioxide solution on a Varian A-60A spectrometer with tetramethylsilane as internal standard. The multiplicity of the signal is given by s for singlet, d for doublet, q for AB quartet, h for heptet, and m for unresolved multiplet.

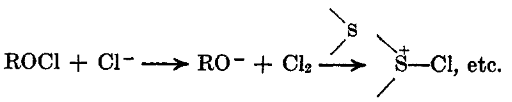
fonium chlorides were too unstable to be isolated but could be transformed to the more stable and readily isolable hexachloroantimonates by the addition of antimony pentachloride. The salts were characterized by elemental analyses (Table I) and nmr (Table II).



It is our contention that alkyl hypohalite and other oxidations of sulfides by positive halogen compounds involve the formation of halosulfonium salts.[7] Oae and co-workers[8] have suggested that an initial bromosulfonium salt is formed in the oxidation of sulfides to sulfoxides by N-bromosuccinimide (NBS) in aqueous solution. A degree of parallelism in these positive



and/or



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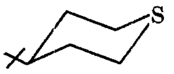
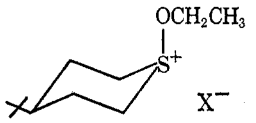
[7] In a forthcoming paper we will provide detailed commentary on stereochemistry and mechanism of oxidation of sulfides with positive halogen compounds.

[8] W. Tagaki, K. Kilukawa, K. Ando, and S. Oae, *Chem. Ind.* (London), 1624 (1964).

halogen oxidations is exhibited in the oxidation of 4-*t*-butylthiane (III) in ethanol solution by NBS followed by addition to silver tetrafluoroborate, or by *t*-butyl hypochlorite followed by addition of silver tetrafluoroborate or mercuric chloride. In each case salt IV (as the fluoroborate or trichloromercurate) was obtained as the major product.[9]



III



IV

Experimental Section

General Procedure for Preparation of *t*-Butoxy- and Isopropoxysulfonium Hexachloroantimonates.—To a solution of the sulfide (0.01 mole) in 20 ml of methylene chloride at −78° was added 1 equiv of alkyl hypochlorite (*t*-butyl hypochlorite was added neat; isopropyl hypochlorite was added as a methylene chloride solution maintained at −78°). After 15 min 1.28 ml (0.01 mole) of antimony pentachloride was added to the stirring solution. The solution was allowed to stir for another 10 min before addition of anhydrous ethyl ether to the cloud point. The solution was allowed to warm to 0°. The resultant precipitate was collected by filtration and recrystallized from methylene chloride–ethyl ether. The salts were dried in a vacuum desiccator unless they had been found to be unstable, in which case they were pressed dry on a sintered-glass Büchner funnel and stored immediately at 0°.

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[9] C. R. Johnson and D. McCants, Jr., unpublished results.

Spectroscopic Studies of Ketol–Enol Equilibria. XI. Optical Rotatory Dispersion in Aromatic Schiff Bases[1]

GERALD DUDEK

Department of Chemistry, Harvard University, Cambridge 38, Massachusetts

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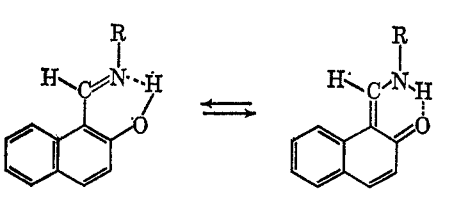
There is considerable influence of keto–enol equilibria (Ia ⇄ Ib) on the optical rotatory activity of Schiff bases



Ia Ib

derived from aromatic carbonyl compounds and optically active amines. In Figure 1, the complex optical rotatory dispersion (ORD) spectrum of a typical compound, I [R = (*S*)-(+)-α-phenylethyl] is depicted for three solvents.[2] The solvents were chosen, with reference to the pmr studies on similar systems,[1,4] to cover a range of associating ability. Above 320 mμ, the ORD curve is strongly solvent dependent with the curve in hexane differing markedly from the two for the hydrogen-bonding solvents, chloroform and absolute ethanol.

With compounds of this type, the proton can reside on either oxygen (Ia) or nitrogen (Ib) and this equilibrium has been extensively studied by means of proton resonance spectroscopy utilizing ^{15}N-labeled amines.[1,4] The pmr data indicate the equilibrium is toward Ia in nonpolar solvents, while in hydrogen-bonding solvents the equilibrium is shifted markedly toward Ib, the nonaromatic tautomer. In naphthols (1,2 substituted), the equilibrium is toward Ib, while in phenols the equilibrium is largely toward forms similar to Ia. Therefore the curves of Figure 1 are a result of the shift of the proton from oxygen to nitrogen as the solvent becomes more associating.[1] The dearomatization of the aromatic system accompanying the tautomer shift produces an extremum of the Cotton effect at considerably longer wavelengths.

The ultraviolet absorptions of the Schiff base (I, $R = CH_3$) consists of several solvent-dependent bands in the long wavelength region. One band at 350 mμ has been assigned to the aromatic tautomer Ia, while a pair at 408 and 420 mμ ($CDCl_3$ solution) has been assigned to the nonaromatic form, Ib.[1,5] The origin of the 318-mμ band (seen at 315 in salicylaldimines) is not known.[3] The band is not markedly solvent dependent, but does appear to involve the Schiff base chromophore.

From the ultraviolet spectrum of I in hexane solution, it can be determined that a small amount of Ib is present since the intensity of the 420-mμ band in hexane is 11% of its intensity in absolute ethanol. This is consistant with the data in Figure 1 and indicates that the ORD curve of Ia has no extremum beyond 350 mμ.

In their studies of optically active salicylaldimines, Smith and his colleagues[3] noted anomalies in the ORD curves of these Schiff bases as compared to the benzylidine derivatives. In particular, a new weak Cotton effect, centered at 420 mμ, appeared in ethanol solutions of the salicylaldimines. These authors discussed several possible explanations, and with the assistance of the ^{15}N pmr data, this anomaly clearly is the result of the presence of about 10% of the nonaromatic form (similar to Ib) in ethanol solution. The value for the molecular rotation $[\Phi]$ observed here is consistent with those reported by Smith, *et al.*,[3] if a correction is made for the amount of ketamine present in the solution.

With the results of the compound discussed here, which is a typical member of the naphthalene series, and the data of Smith on the phenols, it can be seen that the shift of the proton from one site to the other profoundly alters the electronic environment about the nitrogen. The reorganization most likely includes the aromatic system. The fact that the chromophore is quite disymmetric results in large rotations being observed.[6] If the integrated areas were used, the difference in rotatory power between Ia and Ib would be larger owing to the greater breadth of the 400-mμ bands compared with the 370-mμ band from Ia.

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[1] Part X: G. Dudek and E. P. Dudek, *Tetrahedron*, in press.

[2] For compatibility with the data of Smith, *et al.*,[3] the figure is given for the (+) isomer, although the (−) isomer was actually used.

[3] H. E. Smith, S. L. Cook, and M. E. Warren, *J. Org. Chem.*, **29**, 2265 (1964); M. E. Warren and H. E. Smith, *J. Am. Chem. Soc.*, **87**, 1757 (1965); H. E. Smith and R. Records, *Tetrahedron*, **22**, 813 (1966).

[4] G. Dudek and E. P. Dudek, *Chem. Commun.*, 464 (1965); *J. Am. Chem. Soc.*, **88**, 2407 (1966).

[5] There is a distinct inflection in the ORD curve at 415 mμ, corresponding to the minimum in the ultraviolet spectrum between the 408- and 420-mμ bands.

[6] *Cf.* P. Crabbe and B. Halpern, *Chem. Ind.* (London), 346 (1965).