diazomethane were mixed at −78° and allowed to warm slowly to room temperature. Distillation gave 3.57 g (96%) of **4** as a colorless liquid: bp 44–45° (20 mm); $n^{25}{}_D$ 1.3622; ^{19}F nmr (neat) δ 57.3 ppm (q, *J* = 8 Hz, 3 F), 63.2 (q, *J* = 8 Hz, 3 F), 70.7 (s, 6 F); ir (liquid) 6.17 and 6.48 μ (C=C and N=N); Raman, 1630 and 1552 cm^{-1}; uv (isooctane) λ_{max} 327 mμ (ε 4200).

Anal. Calcd for $C_7F_{12}N_2S$: C, 22.59; F, 61.27; N, 7.53; S, 8.61. Found: C, 22.89; F, 61.67; N, 7.67; S, 8.67.

2,2-Bis(trifluoromethyl)-3-bis(trifluoromethyl)methylenethiirane (5).—A 2.0-g sample of **4** was heated at reflux for 24 hr and then distilled to give **5** as a colorless liquid: bp 93°; $n^{25}{}_D$ 1.3279; ir (liquid) 5.75 μ (C=C); uv (ethanol) λ_{max} 239 mμ (ε 11,400), ^{19}F nmr (neat) δ 61.0 ppm (m, 3 F), 63.0 (q, *J* = 6 Hz, 3 F), 67.4 (q, *J* = 4 Hz, 6 F).

Anal. Calcd for $C_7F_{12}S$: C, 24.43; F, 66.25; S, 9.32. Found: C, 24.55; F, 66.32; S, 9.23.

Registry No.—**1,** 684-23-1; **2,** 20728-38-5; **3,** 2375-87-3; **4,** 20708-15-0; **5,** 20728-39-6.

1,2 and 1,4 Addition of Ethylene to Butadiene

RICHARD K. LYON

Corporate Research Laboratories,
Esso Research and Engineering Company,
Linden, New Jersey 07036

Received January 28, 1969

In a recent paper[1] Bartlett and Schueller report that at 175° the addition product of ethylene to butadiene consisted of 99.98% cyclohexene (CH) and 0.02% of a second product. Since this second product had the same retention time on two gas chromatographic columns as authentic vinylcyclobutane (VCB), they identify it as VCB. The conditions of the experiment were such that the product ratio, CH/VCB, is equal to the ratio of rate constants $k_{1,4}/k_{1,2}$ where $k_{1,4}$ and $k_{1,2}$ are the rate constants for formation from ethylene and butadiene of CH and VCB, respectively. The authors discuss the implications of this new reaction to the mechanism of the Diels–Alder reaction. It is the purpose of this paper to point out that there exist data in the literature from which the value of $k_{1,4}/k_{1,2}$ can be independently calculated.

The author feels the calculation is of interest both because it confirms Bartlett and Schueller product identification and because it provides new information, the temperature dependence of $k_{1,4}/k_{1,2}$.

It can easily be shown that $k_{1,4}/k_{1,2} = (k_{-1,4}/k_{-1,2})\ K_3$ where $k_{-1,4}$ and $k_{-1,2}$ are the rate constants for decomposition to ethylene and butadiene of CH and VCB, respectively, and K_3 is the equilibrium constant for the isomerization of VCB to CH. Using the tables given by Benson,[2] one calculates, *via* the group additivity method, that $\log K_3 = -1.604 + (25500/4.57\ T)$.

Uchizama, Tomioka, and Amano[3] report that $\log k_{-1,4} = 15.16 - (66200/4.575\ T)$. $k_{-1,2}$ has not been measured directly but it should be very nearly equal to the rate at which isopropenylcyclobutane[4] decomposes to ethylene and isoprene; *i.e.*, $\log k_{-1,2} = 14.64 - (51030/4.575\ T)$. This assumes that introducing a methyl group in a next nearest neighbor position does not change the rate of cyclobutane ring rupture. This assumption may be justified by comparing the rate constants of decomposition of methyl cyclobutane[5] and ethyl cyclobutane.[6] At 450° they are 7.6×10^{-4} sec^{-1} and 6.6×10^{-4} sec^{-1}, respectively. Thus one calculates that $\log k_{1,4}/k_{1,2} = 1.08 + (10350/4.575\ T) = 3.97$ at 175°, in good agreement with Bartlett and Schueller's value of 3.7.

Registry No.—Ethylene, 74-85-1; butadiene, 106-99-0.

---

[1] P. D. Bartlett and K. E. Schueller, *J. Amer. Chem. Soc.*, **90**, 6071 (1968).

[2] S. W. Benson, "Thermochemical Kinetics," John Wiley & Sons, Inc., New York, N. Y., 1968.

[3] M. Uchizama, T. Tomioka, and A. Amano, *J. Phys. Chem.*, **68**, 1878 (1964).

[4] R. J. Ellis and H. M. Frey, *Trans. Faraday Soc.*, **59**, 2076 (1963).

[5] M. N. Das and W. D. Walters, *Z. Physik. Chem.* (Frankfurt), **15**, 22 (1958).

[6] R. E. Wellman and W. D. Walters, *J. Amer. Chem. Soc.*, **79**, 1542 (1957).

Thiabenzenes. VI. Steric Factors Influencing the Stability of 2-Phenyl-2-thianaphthalenes

CHARLES C. PRICE AND DOUGLAS H. FOLLWEILER[1]

Department of Chemistry, University of Pennsylvania,
Philadelphia, Pennsylvania 19104

Received January 7, 1969

The first thiabenzene prepared, the 1,2,4,6-tetraphenyl compound,[2a] was relatively unstable compared to others prepared later.[2b,c] While it failed to protonate readily like the phosphorabenzenes,[3] it rearranged to the isomeric thiopyran and reacted readily with oxygen. These differences in stability, as well as a difference in color, the unstable analog being purple while all the stable compounds were red-brown, was rationalized on the basis of a hypothesis that there was very little, if any, barrier to out-of-plane bending at phenyl–sulfur bond in these molecules due to relatively equal energy p^3 and sp^2 bonding geometry at the sulfur atom in thiabenzenes.[2b,c,3] This low barrier to bending was also offered as an explanation for the amorphous nature of these compounds as well as their remarkably broad absorbance of visible and ultraviolet radiation.

In order to test these theories further, we have now prepared two hindered analogs of the stable thiabenzene, 2-phenyl-2-thianaphthalene, by the following synthetic route, taking advantage of the fact that, while phenyllithium generally couples on the sulfur of thiopyrylium salts,[2] the Grignard reagent couples on carbon.

For the case of R = *t*-Bu, it was not possible to isolate the thianaphthalene IVb. Reaction mixtures for its preparation were deep wine red or purple (although the color faded in a day or so), but quenching with aqueous ammonium chloride gave the protonated form, Vb, as colorless crystals. This salt could be deprotonated only by base as strong as potassium ethoxide in DMSO, indicating a pK_a in the range of 20–25.

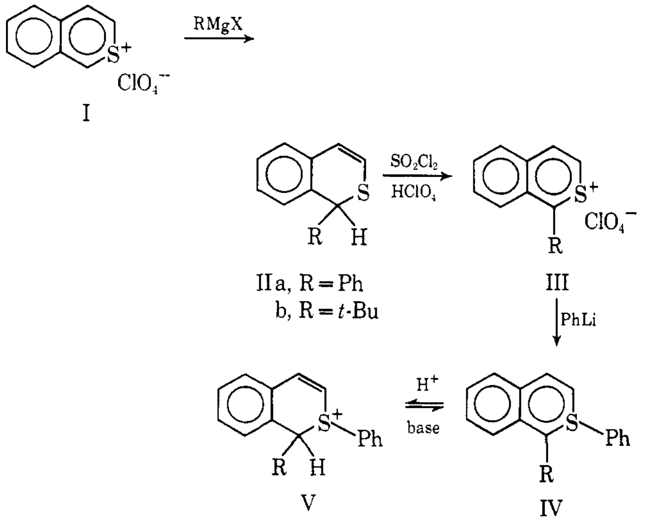
---

[1] Supported in part by a grant from the National Science Foundation, NSF GP-5269.

[2] (a) G. Suld and C. C. Price, *J. Amer. Chem. Soc.*, **83**, 1770 (1961); **84**, 2094 (1962). (b) C. C. Price, M. Hori, T. Parasaran, and M. Polk, *ibid.*, **85**, 2278 (1963). (c) C. C. Price, M. Polk, and M. Siskin, *ibid.*, in press.

[3] G. Markl, *Angew. Chem.*, **75**, 168, 669, 1121 (1963).

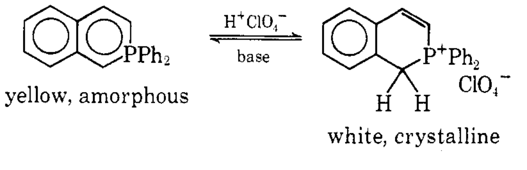
For the case of R = Ph, it was possible to isolate IVa as a purple amorphous solid. It was readily interconvertible to Va, and pH titration indicated a pK_a of 2.9.



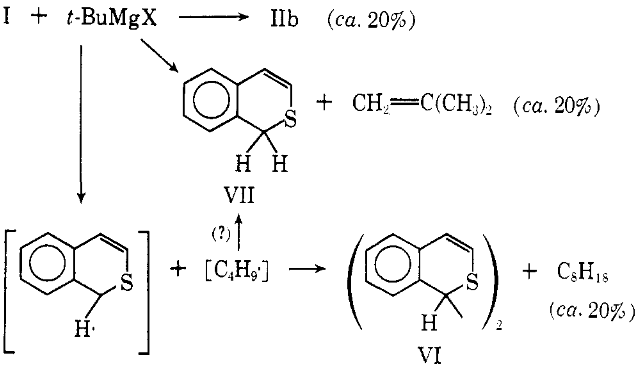
While the color of solutions of IVb faded in a day or so, even under nitrogen, the color of solutions of IVa faded only slowly in a month under nitrogen, although oxygen discharged the color rapidly. This latter property is similar to that of 1,2,4,6-tetraphenylthiabenzene. In fact, the analytical sample of IVa evidently picked up oxygen before it was analyzed.

Since unsubstituted 2-phenyl-2-thianaphthalene is stable to oxygen and to aqueous acids, it seems clear that steric hindrance in the form of a 1-phenyl or 1-*t*-butyl group has a major influence on the stability of this ring system. Since the bulkier *t*-butyl group has the larger influence, it does seem that a steric factor is a reasonable explanation. The great steric influence of a single substituent *ortho* to the S-phenyl group in this system may be due to the buttressing effect of the *peri* hydrogen.

The destabilization caused by the *ortho* hindrance we ascribe to a diminished contribution from the planar sp^2 geometry at sulfur, which permits participation of the 3p orbital on sulfur in the aromatic π bonding. In the sterically favored nonplanar p^3 geometry, only 3d orbitals on sulfur would be free to participate in the aromatic π bonding. It is significant to note that the phosphabenzenes,[3] which also must use 3d orbitals for aromatic π bonding, are also readily and reversibly protonated, even in the absence of *ortho* hindrance.



It is of interest to note that conversion of I to II was accomplished in good yield for R = Ph, but for R = *t*-Bu considerable *one-* and *two*-electron reduction accompanied coupling at position 1. The one-electron reduction produced octane and dimer VI, while two-electron reduction produced isobutylene and 2-thio-3-chromene (VII). The dimer VI was isolated in both the *meso* and the *dl* forms.



Experimental Section

1-Phenyl-2-thio-3-chromene (IIa).—Phenylmagnesium chloride (25 ml, 2.5 *M* in tetrahydrofuran) was added dropwise to a stirred suspension of 10 g of 2-thianaphthalenium perchlorate[4] in 200 ml of ether under nitrogen. After washing, the product distilled at 132–133° (0.15 mm), mp 37–38°.

Anal. Calcd for $C_{15}H_{12}S$: C, 80.31; H, 5.39; S, 14.29. Found: C, 80.21; H, 5.34; S, 14.27.

The uv spectrum in methanol showed λ_{max} (log ϵ) at 207 (4.55), 245 (4.07), and 322 mμ (3.70), while the nmr showed a phenyl multiplet at τ 2.50–3.20 (9 H), two vinyl doublets at 3.43 and 3.93 (J = 10 cps, 1 H each), and a singlet at 4.95 (1 H).

1-Phenyl-2-thianaphthalenium perchlorate (IIIa) was prepared from 3.1 g of IIa in 50 ml of ether by slow addition of 3 ml of sulfuryl chloride in 50 ml of ether at −78°. The orange precipitate was collected cold and resuspended in 100 ml of ether at −78°, and 50 ml of 70% perchloric acid at −30° was added with stirring. The bright yellow crystals were recrystallized from glacial acetic acid to yield 3.07 g (68%) of yellow needles, mp 184–185°.

Anal. Calcd for $C_{15}H_{11}SClO_4$: C, 55.82; H, 3.44; S, 9.93; Cl, 10.98. Found: C, 55.72; H, 3.39; S, 10.03; Cl, 10.83.

This salt showed uv absorbance (methanol) at λ_{max} (log ϵ) 235 (3.94), 242 (3.90), 267 (3.66), 293 (3.81), and 308 mμ (3.80), while the nmr (trifluoroacetic acid) showed a sharp singlet at τ 0.80 (2 H), a multiplet at 1.20–1.67 (4 H), and a singlet at 2.17 (5 H).

1,2-Diphenyl-2-thiochromenium perchlorate (Va) was prepared by adding 3 ml of 2.46 *M* phenylmagnesium chloride in THF dropwise to a slurry of 1 g of IIIa in 25 ml of ether under nitrogen. The purple solution was quenched with aqueous ammonium chloride, precipitating 0.52 g (42%) of Va, mp 160° dec. It recrystallized from glacial acetic acid as colorless plates.

Anal. Calcd for $C_{21}H_{17}SClO_4$: C, 62.92; H, 4.27; S, 8.00; O, 15.96; Cl, 8.84. Found: C, 62.74; H, 4.34; S, 7.97; O, 15.99; Cl, 8.67.

This compound showed uv absorbance at λ_{max} (log ϵ) 202 (4.67) and 285 (4.13), and nmr bands at τ 1.62 (doublet, J = 9 cps, 1 H),[5] 1.97–2.93 (multiplet, 14 H), 3.12 (singlet, 1 H), and 3.20 (doublet, J = 9 cps, 1 H).[5]

1,2-Diphenyl-2-thiabenzene (IVa) was isolated from reaction of 1 g of IIIA in 50 ml of ether with 5 ml of 0.91 *M* phenyllithium in ether at −78°. When this purple reaction mixture was quenched with aqueous ammonium chloride, the purple color was not destroyed, although 0.37 g of Va precipitated, mp 159–160° dec. Further washing and then evaporation of the ether left 0.39 g of IVa as a purple amorphous solid softening at 60–100°. Compound IVa showed only broad aromatic absorbance at τ 2.2–3.4 in the nmr spectrum. Analysis indicated that this material, like 1,2,4,6-tetraphenylthiabenzene,[2a] picked up oxygen.

Anal. Calcd for $C_{21}H_{16}SO$: C, 79.60; H, 5.08; S, 10.10. Found: C, 79.00; H, 4.86; S, 10.56.

The uv spectrum showed a continuous increase in absorbance from 350 to 220 mμ with a shoulder at 245 mμ.

It was also possible to convert Va to IVa by base. For example, 131 mg of Va in 50 ml of ethanol was titrated with 5.34 m*M* potassium hydroxide in ethanol[6] using a Beckman pH meter.

---

[4] A. Lüttringhaus and N. Engelhard, *Ber.*, **93**, 1525 (1960).

[5] M. Caserio, R. Pratt, and R. Holland, *J. Amer. Chem. Soc.*, **88**, 5747 (1966), report, for dimethyl β-styrylsulfonium fluoroborate, τ 2.17 for Hβ and τ 3.33 for Hα, with J = 9.5 cps.

[6] R. C. Bates, "Determination of pH, Theory and Practice," John Wiley & Sons, Inc., New York, N. Y., 1960, p 227.

The pH at half-neutralization (pK_a) was 2.9, and the neutralization equivalent was 396 (calcd, 400.6). Purple solutions of Va prepared from IVa by base and kept under nitrogen slowly faded in a month at room temperature.

1-*t*-Butyl-2-thio-3-chromene (IIb) was prepared by treating 30 g of I in 500 ml of ether with 100 ml of 1.48 *M* *t*-butylmagnesium chloride.[7] When the ether layer was quenched with aqueous ammonium chloride, 2.1 g (12%) of white crystalline dimer of I, mp 230–231°, precipitated. The ethe layer was stripped of solvent by distillation; the distillate was found to have glpc peaks corresponding to isobutylene and 2,2,4-trimethylpentane. Addition of a small amount of acetone to the residue gave the isomeric dimer of I, mp 199–200°.[8] The acetone mother liquor was evaporated and vacuum distilled to give a main fraction, bp 120–133° (0.07 mm). Vacuum sublimation of this oil at 0.3 mm at room temperature gave 4.0 g (22%) of liquid 2-thio-3-chromene, and, when the sublimation temperature was raised to 40°, 5.5 g (22%) of IIb, mp 63–64°.

Anal. Calcd for $C_{13}H_{16}S$: C, 76.41; H, 7.89; S, 15.63. Found: C, 76.29; H, 7.75; S, 15.86.

1-*t*-Butylnaphthalenium perchlorate (IIIb) was prepared from IIb by treatment with sulfuryl chloride at −78° (as for IIa). Recrystallization from glacial acetic acid gave light yellow leaflets, mp 196–197°.

Anal. Calcd for $C_{13}H_{15}SClO_4$: C, 51.56; H, 4.99; S, 10.59; Cl, 11.71. Found: C, 51.82; H, 5.00; S, 10.37; Cl, 11.80.

The uv absorbance (methanol) showed λ_{max} (log ϵ) at 205 (4.41), 240 (3.90), 290 (3.57), 302 (3.67) and 320 mμ (3.72), and the nmr (trifluoroacetic acid) showed bands at τ 0.80 (3 H), 1.30–1.83 (3 H), and 7.87 (9 H).

1-*t*-Butyl-2-phenyl-2-thio-3-chromenium perchlorate (Vb) was prepared by treating a slurry of 1 g of IIIb in 50 ml of ether with 5 ml of 2.46 *M* phenylmagnesium bromide in THF. The purple solution was quenched with cold aqueous ammonium fluoride, precipitating 1.11 g (88%) of IVb. Recrystallization from glacial acetic acid gave 0.88 g (70%), mp 169–170°.

Anal. Calcd for $C_{19}H_{21}SClO_4$: C, 59.91; H, 5.56; S, 8.42; O, 16.80; Cl, 9.31. Found: C, 60.03; H, 5.41; S, 8.57; O, 16.84; Cl, 9.26.

The same compound was obtained in 36% yield with phenyllithium. The uv absorbance showed λ_{max} (log ϵ) at 232 (5.34), 275 (3.70), and 297 mμ (3.87), and nmr bands at τ 1.52 (doublet, 1 H, J = 10 cps), 1.90–2.53 (multiplet, 9 H), 2.78 (double doublet, 1 H, J = 10 and 2 cps), 4.93 (doublet, 1 H, J = 2 cps), and 8.73 (9 H).

Efforts to convert IVb to Vb were unsuccessful with potassium hydroxide in ethanol; the pH jumped from 6 to 12 on addition of less than 10% of 1 equiv of base. By reaction with potassium ethoxide or *t*-butoxide in DMSO, however, a port-wine color developed, perhaps due to Va. The color faded in a day or so, as did that of a phenyllithium reaction mixture.

Registry No.—IIa, 20707-97-5; IIb 20707-98-6; IIIa, 20728-45-4; IIIb, 20707-99-7; IVa, 20708-00-3; Vb, 20708-01-4; Va, 20708-02-5.

(7) "Organic Syntheses," Coll. Vol. I, John Wiley & Sons, Inc., New York, N. Y., 1941, p 524.

(8) Structure proof, properties, and other methods of preparation of these *meso-* and *dl*-1,1 dimers of I are described in theses by M. Siskin and C. K. Miao, Department of Chemistry, University of Pennsylvania.

Reactions of Alkyl Halides in Amides Containing Water or Ammonia

Joseph S. Matthews and Jane P. Cookson

Gulf Research & Development Company,
Pittsburgh, Pennsylvania 15230

Received July 3, 1968

The reaction of alkyl halides with anhydrous acetamide has been reported by Erickson[1] to yield the substituted amide and by Joyce[2] to yield esters. Bredereck[3] and coworkers reported that the reactions of anhydrous formamide with alkyl halides yield formates or substituted formamides depending on the structure of the halide. In all of the above reactions, at least 2 mol equiv of anhydrous amide are required and only primary amides react.

Aqueous Amides.—We wish to report that, in the presence of water, all types of amides react with halides to yield a mixture of the corresponding ester and alcohol (Table I). In addition, only 1 mol of amide is consumed per mol of halide. All types of halides react (Table II) except fluorides, vinylic halides, and halogenated aromatics. The over-all reaction is as follows

Table I

Reaction of Aqueous Amides with *n*-Octyl Bromide

Amide	Bromide conversion, %[a]	Products, %[b]		Temp, °C	Time, hr	A/W/H[c]
		Alcohol	Ester			
$HCONH_2$	100	17.9	80.6	160	1	20:2:1
$HCON(CH_3)_2$	94.8	24.3	70.5	135	2	28:5:1
$CH_3CON(CH_3)_2$	74	49	25	130	3	9:6:1
$C_6H_5CONH_2$	99.4	18.0	79.4	170	3	20:3:1
$HCONHC_6H_5$[d]	99	19.4	79.6	160	2	20:3:1

[a] Based on unreacted bromide recovered. [b] The difference, if any, between % products and % conversion is due to formation of N-alkyl-substituted amides. [c] Molar ratios of amide/water/halide. [d] There was appreciable (5–10%) hydrolysis to aniline also.

Table II

Reactions of Various Halides with Aqueous Formamide[a]

Halide	Halide conversion, %[b]	Temp, °C	Time, hr
$C_8H_{17}Cl$	63	140	3
$C_8H_{17}Br$	100	140	3
$C_8H_{17}I$	100	140	3
$C_6H_{13}CHBrCH_3$	97	140	3

[a] Molar ratio of amide/water/halide, 22:6:1. [b] Products are the corresponding formate–alcohol mixture.

$$RX + R'CONR_2'' + H_2O \longrightarrow R'CO_2R + NR_1''H_2X \quad (1)$$

$$R'CO_2R + H_2O \rightleftharpoons ROH + R'CO_2H \quad (2)$$

where R is alkyl or aralkyl, and R′ and R″ are organic or hydrogen.

By contrast, less than 2% ester–alcohol formed when anhydrous dimethylformamide was refluxed (152°) with *n*-octyl bromide for 3 hr.

For purposes of determining the stoichiometry of the reaction of octyl bromide with aqueous formamide, the distribution of alcohol in the product was determined by acetylation; excess (unreacted) water was determined by Karl Fischer titration; ammonium bromide was determined by titration with standard silver nitrate solution; and the excess formamide was determined by distilling and weighing. No determination of free formic acid, if any, was made. The recovery procedure for the material balance takes advantage of the fact that at room temperature, about 90% of the alcohol–ester product separates as a top layer. This may be

---

(1) J. L. E. Erickson, *Chem. Ber.*, **59B**, 2665 (1926).

(2) R. M. Joyce (to Du Pont Co.), U. S. Patent 2,375,301 (1945).

(3) H. Bredereck, R. Gomper, and G. Theilig, *Chem. Ber.*, **87**, 537 (1954).