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); $n^{25}\text{D}$ 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) $\lambda_{\max}$ 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°; $n^{25}\text{D}$ 1.3279; ir (liquid) 5.75 μ (C=C); uv (ethanol) $\lambda_{\max}$ 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

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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.

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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.

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