as starting from the coiled conformation either by a direct electrocyclic ring opening to 9-methyl-*cis,cis,-cis,cis*-cyclononatetraene or by a preceding Cope rearrangement.[2c–e,11] The finding that the *gem*-dimethyl compound **1d** takes a different path to give 1,1-dimethyl-*trans*-3a,7a-dihydroindene[2e] seemed to question this mechanism. The present work substantiates as the rate-determining step for the rearrangement of **1a–c** a pericyclic reaction from the coiled conformation. By demonstrating that *gem*-9-methyl groups especially oppose such a reaction, it rationalizes the opening of an alternative pathway to **1d** *via* the *gem*-dimethyl-*trans,-cis,cis,cis*-cyclononatetraene.[12]

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[11] A recent review of work done on the rearrangement of *cis*-bicyclo[6.1.0]nona-2,4,6-triene is given by J. E. Baldwin, H. A. Andrist, and R. K. Pinschmidt, Jr., *J. Amer. Chem. Soc.*, **94**, 5845 (1972).

[12] S. W. Staley and T. J. Henry, *ibid.*, **91**, 7787 (1969).

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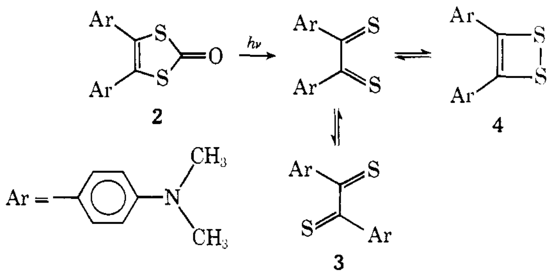
Thione Photochemistry. Preparation of an α-Dithione and the α-Dithione–1,2-Dithiete Equilibrium[1,2]

Sir:

The literature of the last 50 years records a number of attempts to prepare both α-dithiones and 1,2-dithietes.[3] Up to the present no success has been reported with regard to the synthesis of α-dithiones. The preparation of the related α-thionoketone, monothiobenzil, has been achieved,[4,5] as have a group of three polyfluorinated 1,2-dithietes.[6] We now wish to report the synthesis and properties of the first stable α-dithione, 4,4′-bis(dimethylamino)dithiobenzil (**3**), and in particular its equilibrium with the corresponding dithiete (**4**).[7]

The starting material for the synthesis was 4,4′-bis-(dimethylamino)desoxybenzoin,[9] which on treatment with HBr and bromine in glacial acetic acid gave the corresponding acyloin acetate (**1**),[10] mp 142–143°, in 58% yield. Reesterification of **1** with potassium xanthate in ethanol gave the xanthate,[10] mp 153–154° (44%), which was cyclized in anhydrous HF in the presence of H_2S to give the vinylene dithiocarbonate (**2**),[10] mp 215–216°, in 39% yield. Irradiation of a benzene solution of **2** under nitrogen at room temperature with light of wavelength $\lambda > 350$ nm gave 4,4′-bis-(dimethylamino)dithiobenzil (**3**),[10] which slowly crystallized from the irradiated solution in 50% yield. The dithione (**3**) is a dark red crystalline compound, mp 184–185.5°.



The mass spectrum of **3–4** has a large molecular ion at *m/e* 328[11] and the fragmentation pattern is essentially analogous to those observed for **2**, diphenylvinylene dithiocarbonate,[12] and the bis(trifluoromethyl)-1,2-dithiete cation radical.[13] Fragments due to the loss of one or two sulfur atoms give rise to peaks at *m/e* 296 and 264. The structure of **3** follows from its monomeric nature, uv spectrum, and the nature of the equilibrium now to be discussed.

We have found that **3** is, in solution, an equilibrium of the α-dithione form of the molecule **3** and the valence tautomeric form **4**. All spectra taken in solution clearly indicate the presence of two species. Similarly, the presence of two species in solution is indicated by the nmr spectrum of **3–4** which shows two singlets at 3.07 and 2.95 ppm. That at 3.07 ppm is assigned to the dimethylamino group in **3**, while the corresponding group in **4** absorbs as expected at somewhat higher field at 2.95 ppm. The aromatic protons in **3** give rise to an AB system with resonances at 6.53 and 8.06 ppm, the resonances of the corresponding protons in **4** are at 6.59 and 7.21 ppm. Integration over the methyl signals reveals the ratio **3**:**4** = 6:1 in $CDCl_3$ at room temperature.

This equilibrium between **3** and **4** is dependent upon (a) the solvent, (b) light, and (c) temperature. The influence of these three parameters was shown by uv spectroscopy.

Figure 1 shows the absorption spectra of **3** in mixtures of methylene chloride–hexane at room temperature. The high-intensity band with λ_{max} at 470 nm is due mainly to the open form (**3**). It can be seen that this band decreases with decreasing polarity of the solvent, thus

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[1] Photochemical Synthesis. 52. This is No. 11 in a series on thione photochemistry.

[2] Publication No. 67 from the Photochemistry Unit, The University of Western Ontario.

[3] P. C. Guha and M. N. Chakladar, *Quart. J. Indian Chem. Soc.*, 2, 318 (1925); (b) S. K. Mitra, *J. Indian Chem. Soc.*, **15**, 58 (1938); (c) L. Field, W. D. Stephens, and E. L. Lippert, Jr., *J. Org. Chem.*, **26**, 4782 (1961); (d) R. Mayer and M. Nitzschke, *Chem. Ber.*, **96**, 2539 (1963); (e) G. N. Schrauzer and H. W. Fink, *Angew. Chem.*, **76**, 143 (1964); (f) H. E. Simmons, R. D. Vest, D. C. Blomstrom, J. R. Roland, and T. L. Cairns, *J. Amer. Chem. Soc.*, **84**, 4746 (1962); (g) H. E. Simmons, D. C. Blomstrom, and R. D. Vest, *J. Amer. Chem. Soc.*, **84**, 4756, 4772, 4782 (1962).

[4] D. C. Dittmer, G. C. Levy and G. E. Kuhlmann, *J. Amer. Chem. Soc.*, **89**, 2793 (1967); (b) D. C. Dittmer and G. E. Kuhlmann, *J. Org. Chem.*, **35**, 4224 (1970); (c) D. C. Dittmer, G. E. Kuhlmann, and G. C. Levy, *J. Org. Chem.*, **35**, 3676 (1970).

[5] B. Saville and M. Steer, *J. Chem. Soc., Chem. Commun.*, 616 (1972).

[6] C. G. Krespan, B. C. McKusick, and T. L. Cairns, *J. Amer. Chem. Soc.*, **82**, 1515 (1960); (b) C. G. Krespan, *J. Amer. Chem. Soc.*, **83**, 3434, 3438 (1961).

[7] In contrast, 1,2-dithiones are well known as ligands in complexes with transition metals[8] from which, as yet, no method has been found to liberate and isolate the free dithione.

[8] G. N. Schrauzer and V. P. Mayweg, *J. Amer. Chem. Soc.*, **87**, 1483 (1965).

[9] M. G. Allen, *J. Amer. Chem. Soc.*, **73**, 1841 (1951).

[10] All new compounds had C, H, N, and S analyses and spectral data consistent with the proposed structures.

[11] The molecular weight obtained osmometrically in chloroform was 350 ± 8, indicating that the substance is truly a monomer and not a dimer or oligomer decomposed under the vaporization conditions in the mass spectrometer. If the probe temperature in the spectrometer was raised over 100°, peaks at higher masses were observed due to decomposition of the sample. A spectrum run at a probe temperature of 235° does not show the molecular ion any more.

[12] The preparation of this compound will be described elsewhere.

[13] C. G. Krespan and D. C. England, *J. Org. Chem.*, **33**, 1850 (1968).

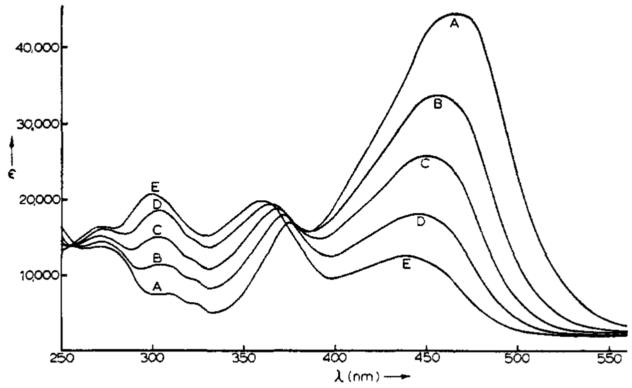

Figure 1. Absorption spectra of equimolar solutions of **3** in solvent mixtures of CH_2Cl_2–C_6H_{14} at room temperature. Volume % C_6H_{14} in CH_2Cl_2: A, 0; B, 52; C, 72; D, 84; E, 92.

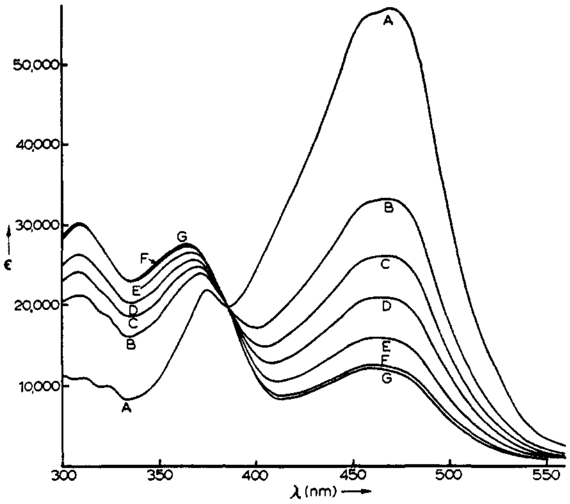

Figure 2. Spectral changes upon irradiation (λ >500 nm) of a degassed solution of **3** in CH_2Cl_2 at −0.4°. Total irradiation time (in sec): A, 0; B, 5; C, 10; D, 20; E, 45; F, 525; G, 3525.

shifting the equilibrium in favor of the dithiete (**4**). Similar effects were obtained in solvent mixtures C_2H_5OH–C_6H_6, C_2H_5OH-*n*-hexane, and CH_3CN–CCl_4.[14] The effect of light on the equilibrium $\mathbf{3} \rightleftarrows \mathbf{4}$ can be deduced from Figure 2. The position of the equilibrium in CH_2Cl_2, which has an equilibrium constant of $K(\mathbf{3}/\mathbf{4}) = 16$ at −0.4°, is approximately reversed after irradiation for 2 min at that temperature with the attainment of a photostationary state.[15] Furthermore the equilibrium returns to its original position, if the solution is allowed to stand in the dark at that temperature. All absorption spectra taken during the irradiation and thereafter go through an isosbestic point (at 385 nm), as one would expect for an equilibrium of this kind.

Kinetic and thermodynamic measurements were carried out by means of uv and nmr techniques between −3 and 43° in order to determine the activation parameters in CH_2Cl_2. It was shown that the tautomerization process cleanly follows reversible first-order kinetics, a fact that clearly excludes the reversible formation of any dimer. The rate constants k_1 ($\mathbf{4} \rightarrow \mathbf{3}$) and k_{-1} ($\mathbf{3} \rightarrow \mathbf{4}$) fit the Arrhenius equations. The values of the

$$k_1 = 4.32 \times 10^{10} \exp\left(-\frac{17.5 \text{ kcal mol}^{-1}}{RT}\right) \text{sec}^{-1}$$

$$k_{-1} = 2.29 \times 10^{13} \exp\left(-\frac{22.4 \text{ kcal mol}^{-1}}{RT}\right) \text{sec}^{-1}$$

equilibrium constants at different temperatures yield the enthalpy change for $\mathbf{4} \rightarrow \mathbf{3}$ as $\Delta H° = -4.9$ kcal mol^{-1} together with $\Delta S° = -12.5$ eu. The activation energy for the ring opening of **4** to **3** is about 15 kcal smaller than average values reported for the ring opening of cyclobutenes to butadienes.[16] This decrease is obviously mainly due to the difference in the bond energies between the C–C and the S–S bonds. For the ring closure $3 \rightarrow 4$ there are only few data available for comparison.[17] The small size of the activation energy, however, suggests that the ring closure is facilitated by a considerable delocalization of the π electrons in the ring.

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(14) It seems likely that the observations of Saville and Steer[6] on monothiobenzil are not due to reversible polymerization of this compound, but originate from valence tautomerization to the oxathiete isomer. The isosbestic point at 470 nm appears to support this assumption.

(15) This was shown by irradiating a sample in an nmr tube at −60° and following the ratio of the methyl peaks of the two isomers.

(16) R. Criegee, D. Seebach, R. E. Winter, B. Börretzen, and H. A. Brune, *Chem. Ber.*, **98**, 2339 (1965); (b) H. M. Frey, *Advan. Phys. Org. Chem.*, **4**, 147 (1966).

(17) E. W. Schlag, and W. B. Peatman, *J. Amer. Chem. Soc.*, **86**, 1676 (1964); (b) J. P. Chesick, *ibid.*, **88**, 4100 (1966); (c) G. A. Doorakian, and H. H. Freedman, *J. Amer. Chem. Soc.*, **90**, 3582 (1968).

(18) Holder of a Canada Council Fellowship, 1972–1973.

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Fluxional Behavior of $B_{11}H_{11}^{2-}$

Sir:

Isomerization of $B_nH_n^{2-}$ ions is generally believed to be a high-temperature phenomenon. We report here the spontaneous isomerization of $B_{11}H_{11}^{2-}$ and of $B_{11}H_7Br_4^{2-}$ ions in solutions at low temperatures in nmr time scales.

The $(Et_4N)_2B_{11}H_{11}$, prepared by known procedures,[1,2] was shown by tlc to have negligible traces of $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$. The $(Me_4N)_2B_{11}H_7Br_4$ was prepared under N_2 by adding dropwise 47.2 mmol of Br_2 in 150 ml of 1 *N* NaOH to 12.4 mmol of $Na_2B_{11}H_{11}$ in 50 ml of 1 *N* NaOH at 2°. After 4 hr at 2° and 20 hr at 25°, 45 ml of a 25% solution of Me_4NOH was added. The precipitate was fractionally recrystallized eight times from 0.1 *N* NaOH and EtOH. *Anal.* Calcd: C, 16.18; H, 5.26; B, 20.02; Br, 53.82; N, 4.72. Found: C, 16.01; H, 5.65; B, 19.57; Br, 53.86; N, 4.81. Also, $(Ph_4As)_2B_{11}H_{11}$ and $(Ph_4As)_2B_{11}H_7Br_4$ were prepared by adding $Ph_4As^+Cl^-$ to aqueous solutions of the sodium salts and then drying the precipitate.

The ^{11}B spectra of the $(alkyl)_4N^+$ salts in a DMF–acetone–methanol solution were taken at 32.1 MHz on a Varian XL-100 spectrometer with Fourier transform. The ^1H spectra of the Ph_4As^+ salts in perdeuteriodimethylformamide–methanol were obtained at 100 MHz on a Varian HA-100 with Fourier transform.

The ^{11}B spectrum of $B_{11}H_{11}^{2-}$ shows a doublet at 16.95 ppm [J(B–H) = 130 Hz] relative to $BF_3 \cdot O(Et)_2$.

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(1) (a) F. Klanberg and E. L. Muetterties, *Inorg. Syn.*, **11**, 25 (1968); (b) F. Klanberg and E. L. Muetterties, *Inorg. Chem.*, **5**, 1955 (1966).

(2) R. L. Middaugh and R. J. Wiersema, *Inorg. Chem.*, **10**, 423 (1971).