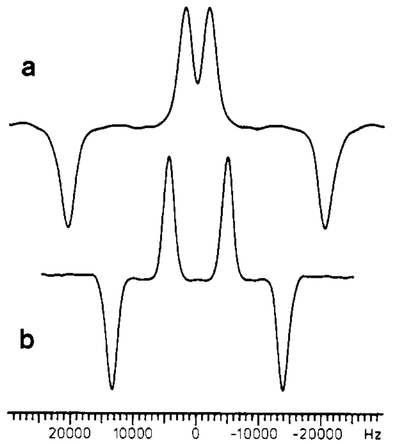

Figure 2. Sections through phase-sensitive ^{15}N 2D SINEPT spectra of pyridine obtained with simultaneous θ_1, θ_2 incrementation and employing $N = 32$ zero-filled to 32K. (a) $\kappa = 1.0$, $\Delta t_1 = 16.7$ μs; (b) $\kappa = 0.4$, $\Delta t_1 = 20.0$ μs.

pulse width. The total recording time for 2D SEMUT with concentrated samples and $N = 32$ is a few minutes.

Pulse sequence 1 should not be employed if polarization transfer enhancement is essential for sensitivity reasons. In addition, the sequence is unsuitable for calibration via long-range couplings because complicated multiplet patterns may occur. ^{15}N NMR of pyridine is an example where polarization transfer enhancement and calibration via long-range couplings are required. For this purpose we introduce the 2D version of INEPT[14,15] or SINEPT:[19]

$$\begin{array}{ll} I(^1\mathrm{H}): & \theta_{2x} - \frac{\tau}{2} - (180°) - \frac{\tau}{2} - \beta_y - \tau' - \text{decouple} \\ S(^{15}\mathrm{N},^{13}\mathrm{C}): & -\frac{\tau}{2} - (180°) - \frac{\tau}{2} - \theta_1 - \tau' - (180°) - \tau' - \text{acquire} \end{array} \quad (3)$$

The refocusing pulses in parentheses should be employed if approximate knowledge about the rf field strengths is available.[22] β is adjusted to the estimated value for a 90° rotation (not critical). The delays τ and τ' are selected as for INEPT[14,15] when one-bond couplings are exploited. Otherwise, $\tau = \tau' = (4J)^{-1}$, where J is the largest relevant homo- or heteronuclear long-range coupling constant. Incrementation of one of the θ pulses while keeping the other constant ($\sim$90°) leads to an antiphase doublet with splitting determined by the corresponding rf field strength.

Here we demonstrate the experiment with simultaneous incrementation of θ_1 and θ_2 which results in a doublet of doublet four-line pattern in the ω_1 dimension of the 2D spectrum. The apparent "J splittings" reflect the rf field strengths of the applied two fields. To avoid overlap of the four components, one of the doublet splittings may be scaled, e.g., by incrementing θ_1 according to $\theta_1 = \kappa\theta_2$. The relevant section through the 2D ^{15}N spectrum of pyridine by using $\kappa = 1.0$ and 0.4 is shown in Figure 2. This experiment yields $t_{90}(^1\mathrm{H}) = 26.4 \pm 0.2$ μs and $t_{90}(^{15}\mathrm{N}) = 22.1 \pm 0.2$ μs which compare favorably with 1D[19] results: $t_{90}(^1\mathrm{H}) = 26.2 \pm 0.3$ μs and $t_{90}(^{15}\mathrm{N}) = 22.1 \pm 0.3$ μs.

We should note that instrumental imperfections can affect the results of the 2D calibration techniques. It is therefore recommended, once and for all, to compare the 2D result with the result of a detailed equivalent 1D calibration.[19] This yields a scaling factor to put on future rf field strengths determined by the 2D techniques.[23] As a consequence, instrumental imperfections are unimportant for routine applications of the presented techniques.[24]

In conclusion, we have in this paper introduced simple 2D pulse techniques for calibration of rf field strengths with significantly higher sensitivity and shorter performance time than 1D methods yielding equivalent information. The time saving can easily reach an order of magnitude for samples of low inherent sensitivity. The multiplicity information in ^{13}C 2D SEMUT spectra makes the performance of separate editing experiments[16-18] superfluous, which results in additional time saving. Furthermore, the ideas presented in this paper can be extended to the more sensitive heteronuclear "inverse" experiments with proton detection.

Acknowledgment. The use of the facilities at the University of Aarhus NMR Laboratory sponsored by the Danish Research Councils (SNF and STVF) and Carlsbergfondet is acknowledged. O.W.S. thanks Professor R. R. Ernst for support and encouragement.

Registry No. Menthol, 89-78-1; pyridine, 110-86-1.

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[22] Inaccurate 180° pulses do not affect the calibration. To improve sensitivity the S spin 180° pulses can be replaced by composite pulses.

[23] On modern spectrometers (e.g., the Varian XL-300 applied in this research) such scaling factors are close to 1.

[24] Sørensen, O. W.; Nielsen, N. C.; Bildsøe, H.; Jakobsen, H. J. *J. Magn. Reson.* **1986**, *70*, 54.

Thiocarbonyl *S*-Sulfides, a New Class of 1,3-Dipoles[†]

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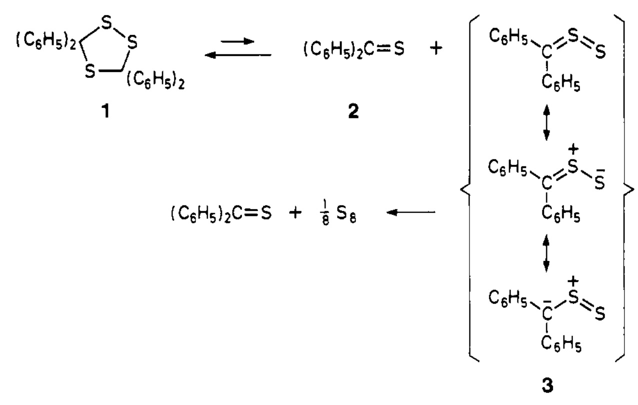
The rich literature on "thiosulfines", $R_2C{=}S{=}S$,[1] oddly contrasts the scant experimental observations of their transient occurrence. In our opinion, this report offers the first unequivocal evidence for their existence.

According to Staudinger,[2] 3,3,5,5-tetraphenyl-1,2,4-trithiolane (**1**) decomposes above the mp 124 °C to give thiobenzophenone (**2**) and sulfur. $\Delta H^\circ_f = 92.0$ kcal mol^{-1} for singlet sulfur atom, S($^1D_2$),[3] forbids a concerted fragmentation into two thiobenzophenones and an S atom. Instead, a 1,3-dipolar cycloreversion may furnish thiobenzophenone *S*-sulfide (**3**) and **2**. In the absence of reaction partners, the molecules of **3** may undergo mutual transfer of the terminal sulfur; long sulfur chains are built up which may roll around and eliminate cyclooctasulfur. *We succeeded in intercepting both dissociation products by cycloaddition.*



Warm solutions of the colorless **1** turn deep blue indicating **2** as dissociation product. After reacting **1** with 4 equiv of dimethyl acetylenedicarboxylate 4 h at 60 °C, ^{1}H NMR analysis indicated 68% of **4** (s, H1, δ 5.14) and 83% of **7** (s, OCH$_3$, 3.41). Chromatography on silica gel separated the colorless 1*H*-2-benzothiopyran derivative **4**, mp 91–92 °C, the Diels–Alder adduct of **2**,[4] and the light-yellow dimethyl 3,3-diphenyl-3*H*-1,2-dithiole-

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[†] Dedicated to Professor Leopold Horner on the occasion of his 75th birthday.

(1) Review articles: (a) Senning, A. In *IUPAC Organic Sulfur Chemistry*; Freidlina, R. K., Skorova, A. E., Eds.; Pergamon: Oxford, 1981; p 151. (b) Kutney, G. W.; Turnbull, K. *Chem. Rev.* **1982**, *82*, 333. (c) Senning, A.; Hansen, H. C.; Abdel-Megeed, M. F.; Mazurkiewicz, W.; Jensen, B. *Tetrahedron* **1986**, *42*, 739. (d) Senning, A. *Sulfur Lett.* **1986**, *4*, 213.

(2) Staudinger, H.; Freudenberger, H. *Ber. Dtsch. Chem. Ges.* **1928**, *61*, 1576, 1836.

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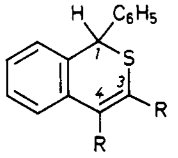
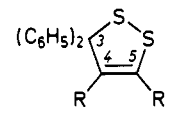
4,5-dicarboxylate (**7**), mp 104 °C,[5] the interception product of **3**. Strongest peaks in the MS of **7** are m/e 308 ($M^+ - 2S$) and 249 (308 − CO_2CH_3), probably originating from **10** and **11**. Desulfurization of **7** by Raney nickel afforded 75% of dimethyl 2-benzhydrylsuccinate (**12**), mp 105–106 °C, identical with a specimen prepared from the Stobbe condensation product **13**[6] by hydrogenation and treatment with CH_3OH/HCl.





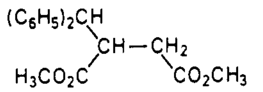
4 R = CO_2CH_3 **7**
5 R = CN **8**
6 R + R = $-(CH_2)_6-$ **9**

$(C_6H_5)_2C{=}C{=}C(CO_2CH_3)_2^{+\cdot}$

10

$(C_6H_5)_2\overset{+}{C}-C{\equiv}C-CO_2CH_3$

11



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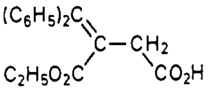
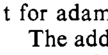


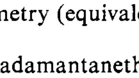
13

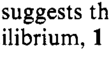
Analogously, the cycloreversion products **2** and **3** were trapped by 2 equiv of dicyanoacetylene (4 h, reflux in $CHCl_3$); chromatography provided the cycloadducts **5** (71%) and **8** (76%). The Diels–Alder adduct **5**, mp 121–122 °C, showed the H1 singlet at δ 5.39 and the expected 12 δ (^{13}C) values for 15 aromatic and olefinic C atoms. As foreseen, three singlets and three doublets appeared for these C atoms in the ^{13}C NMR spectrum of the deep-yellow 1,2-dithiole **8**, mp 132 °C. Likewise, cyclooctyne (3 equiv) combined with **2** and **3** when refluxed with **1** for 4 h in $CHCl_3$. ^1H NMR analysis registered 98% of **6** (s, H1, δ 4.94), mp 66.5 °C. By crystallization, 66% of dithiole **9**, mp 108 °C, was isolated.

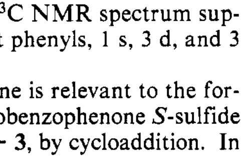
The Diels–Alder adducts **4**–**6** were independently prepared from **2** at 25 °C. The dienophiles are, in order of decreasing reactivity: dicyanoacetylene; cyclooctyne; DMAD. The same sequence of cycloreversion and cycloaddition was carried out with tetrakis(*p*-chlorophenyl)-1,2,4-trithiolane (**14**, mp 130–131 °C dec), using the three intercepting reagents. In contrast, the spiro[bis(fluorene)]-1,2,4-trithiolane (**15**), mp 185–186 °C dec, is stable in boiling $CHCl_3$.



14 R = C_6H_4Cl-(4)

15 R_2 = 

16 R_2 = 

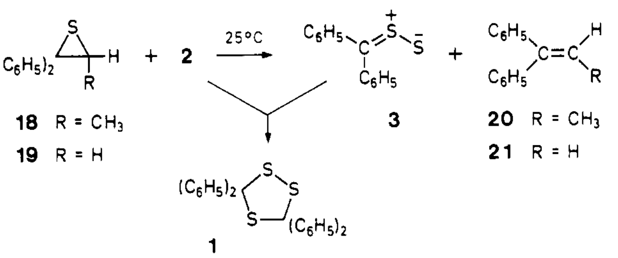


17

Adamantanethione is a dipolarophile, but not an active dienophile. The refluxing solution of **1** and 1.4 equiv of adamantanethione in $CHCl_3$ assumed the deep-blue color of **2**; after 4 h, 81% of the mixed 1,2,4-trithiolane **17** crystallized from pentane, mp 131–132 °C dec (blue melt). The ^{13}C NMR spectrum supports the plane of symmetry (equivalent phenyls, 1 s, 3 d, and 3 t for adamantyl).

The addition of **3** to adamantanethione is relevant to the formation of **3** from **1**. It suggests that thiobenzophenone *S*-sulfide is removed from an equilibrium, **1** $\rightleftharpoons$ **2** + **3**, by cycloaddition. In the conversion of **1** into **17**, thiobenzophenone as the conjugated thione is set free and replaced by the aliphatic thione. Thiobenzophenone *S*-sulfide shares with thiocarbonyl *S*-ylides[7,8] high 1,3-dipolar activity toward thiones; the name thiocarbonyl sulfides was chosen to emphasize the analogy.

Various methods—mechanistically unclear—have been described for the preparation of trithiolane **1** from **2**.[2,9] We report a versatile new method which involves **3** as an intermediate. In the pivotal experiment,[10] thiirane **18** and 2.2 equiv of thiobenzophenone were kept in ether at 25 °C for 24 days; 84% of **1** precipitated and ^1H NMR analysis showed 90% of **20**.

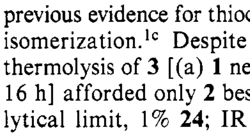


18 R = CH_3
19 R = H
3
20 R = CH_3
21 R = H
1

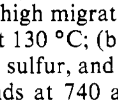
Aromatic thiiranes are capable of *transferring sulfur* to thiones furnishing olefins + thiocarbonyl *S*-sulfides; the latter are captured by 1,3-dipolar cycloaddition to a second mole of the thione providing trithiolanes. Like tertiary phosphanes and phosphites, thiobenzophenone is an active reagent for desulfurization of thiiranes. The reaction of 0.30 M 2,2-diphenylthiirane (**19**) with 2.5 equiv of **2** in $CDCl_3$ at 34 °C was second order with $k_2 = 2.8\ 10^{-5}\ M^{-1}\ s^{-1}$ and reached 92% conversion after 74 h. In the preparative reaction of 0.25 M **19** and 0.60 M **2** in pentane, 92% of **1**, mp 124.5–125 °C, precipitated in 2 weeks at 25 °C, and the solution contained 92% of 1,1-diphenylethylene (**21**) and 3% **19** (^1H NMR). The increasing equilibrium concentration of **3** forbids high reaction temperatures; **19** was quantitatively desulfurized by **2** in 1 h at 100 °C, but no trithiolane **1** remained; TLC indicated S_8. As for the mechanism, we suppose **22** being an intermediate which suffers cheletropic elimination.

Thiirane **19** and 2.0 equiv of thiofluorenone in $CDCl_3$ furnished **15** at 25 °C. 4,4′-Dichlorothiobenzophenone reacts faster than **2** with **19** ($k_2 = 4.5\ 10^{-5}\ M^{-1}\ s^{-1}$). The rate decreased for 4,4′-dimethoxy- and 4,4′-bis(dimethylamino)thiobenzophenone, xanthione, and thioxanthione. Adamantanethione, 2.1 equiv, combined with **19** in 1 h at 100 °C affording 100% **21** and 80% **16**, mp 191–192 °C, which is stable at 100 °C and displays the expected ^{13}C NMR shifts (1 s, 3 d, 3 t) for two adamantyls. In the MS of **16**, m/e 198.050 (100%, calcd for $C_{10}H_{14}S_2$ 198.054) corresponds to the radical cation of adamantanethione *S*-sulfide.

Is thiobenzophenone sulfide (**3**) capable of rearranging via 3,3-diphenyldithiirane (**23**) to phenyl dithiobenzoate (**24**)? The



22



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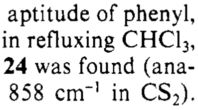

24

previous evidence for thiocarbonyl sulfides rests on such a two-step isomerization.[1c] Despite the high migratory aptitude of phenyl, thermolysis of **3** [(a) **1** neat at 130 °C; (b) **1** in refluxing $CHCl_3$, 16 h] afforded only **2** besides sulfur, and no **24** was found (analytical limit, 1% **24**; IR bands at 740 and 858 cm^{-1} in CS_2).

Acknowledgment. We thank the Fonds der Chemischen Industrie for support.

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