An Unusual Thermal Rearrangement of 5,5,6,6-Tetracyano-2-thiabicyclo[2.2.0]hexane to a Thiophene

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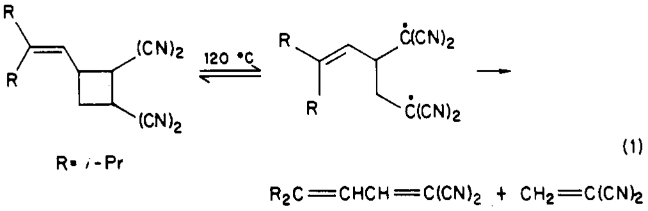
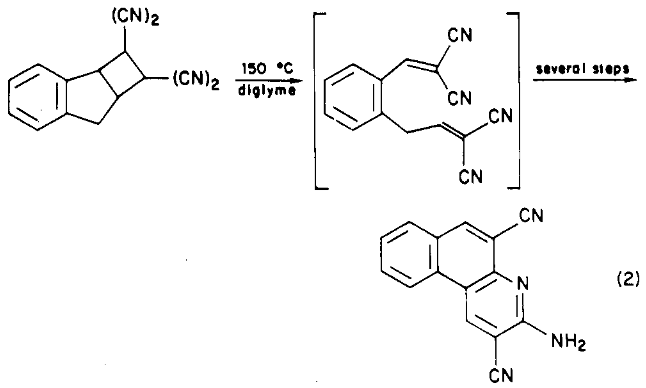
5,5,6,6-Tetracyano-2-thiabicyclo[2.2.0]hexane (2-thiabicyclo[2.2.0]hexane-5,5,6,6-tetracarbonitrile), obtained by cycloaddition of tetracyanoethylene to 2*H*-thiete at room temperature, rearranges in refluxing benzene to 3-amino-4-cyano-2-(2,2-dicyanovinyl)thiophene [[(3-amino-4-cyano-2-thienyl)methylene]propanedinitrile]. The structure of this product was determined by X-ray analysis. Unusually long S–C and C_α–C_β bonds (1.742 and 1.429 Å, respectively) are attributed to resonance between the amino group and the dicyanovinyl group. Addition of anthracene to trap dienophiles in the refluxing benzene solution had no effect on the yield of thiophene. In refluxing acetonitrile, only a small amount of rearrangement product is obtained, the major pathway being cycloreversion to thiete and tetracyanoethylene. The latter can be trapped by anthracene, but the thiete polymerizes under the reaction conditions.

Tetracyanocyclobutanes are thermally labile as exemplified by the fragmentation of 3-(2,2-diisopropylvinyl)-1,1,2,2-tetracyanocyclobutane to 1,1-dicyano-4,4-diisopropyl-1,3-butadiene (eq 1).[1] The cycloadduct of tetracyanoethylene (TCNE) with indene undergoes an unusual thermal rearrangement to 3-amino-2,5-dicyanobenzo[*f*]-quinoline.[2] Thermal cleavage of the cyclobutane ring was suggested as a first step (eq 2). These observations of the instability of tetracyanocyclobutanes are supported by the calculated bond-dissociation energy of 1,1,2,2-tetracyanoethane (39.6 kcal mol^{-1});[3] which is comparable to the oxygen–oxygen bond dissociation energy in alkyl peroxides (ca. 40 kcal mol^{-1}).[4]

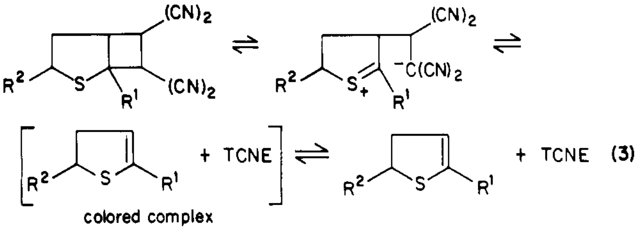


(1)



(2)

In contrast to the above adducts of TCNE with alkenes, the tetracyanocyclobutanes formed by cycloaddition of TCNE with vinyl ethers and vinyl thioethers (eq 3) undergo cycloreversions via zwitterionic intermediates, illustrated for adducts with 2,3-dihydrothiophenes.[5]



(3)

The work reported in this paper was undertaken originally to determine if the adduct of TCNE and 2*H*-thiete could be used as a source of the unstable thiete which could be generated in situ by a cycloreversion such as that shown for the dihydrothiophenes. The TCNE could be scavenged from the solution by a diene which would react with the double bond of the TCNE but not with that of the less dienophilic thiete.

Results and Discussion

5,5,6,6-Tetracyano-2-thiabicyclo[2.2.0]hexane (**1**) is conveniently prepared by treatment of freshly prepared 2*H*-thiete with TCNE in methylene chloride at room temperature. A violet color was observed immediately on mixing solutions of the two reagents; as the color faded to a pale orange, a colorless precipitate of the thiabicyclohexane appeared. This behavior is analogous to that observed in many reactions involving TCNE,[6] such as the cycloaddition to 2,3-dihydrothiophenes cited above.[5] The 360-MHz ^{1}H NMR spectrum of **1** shows a long-range coupling between H^1 and H^4 (J = 1.5 ± 0.2 Hz) attributed to the *M*(or *W*) configuration of the four σ bonds between the two protons. Refluxing adduct **1** in benzene did not cause cycloreversion; instead, an isomer, **2**, was obtained whose structure was established by X-ray analysis as well as by the usual analytical techniques. The adduct **1** is stable to irradiation at −10 °C in methylene chloride (eq 4).

Figure 1 shows a computer-generated perspective drawing of the final X-ray model of **2**. The estimated standard deviation of a bond is approximately 0.01 Å, and this estimate is consistent with chemically equivalent but crystallographically inequivalent bonds. For example, the

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[1] Kataoka, F.; Shimizu, N.; Nishida, S. *J. Am. Chem. Soc.* **1980**, *102*, 711.

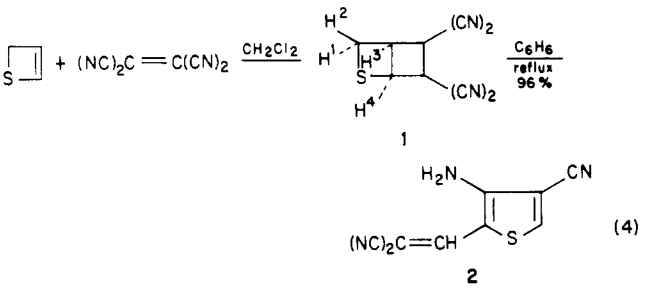
[2] Huebner, C. F.; Strachan, P. L.; Donoghue, E. M.; Cahoon, N.; Dorfman, L.; Margerison, R.; Wenkert, E. *J. Org. Chem.* **1967**, *32*, 1126.

[3] Leroy, G.; Peeters, D.; Wilante, C.; Khalil, M. *Nouv. J. Chem.* **1980**, *4*, 403.

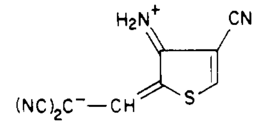
[4] Benson, S. W. *J. Chem. Phys.* **1964**, *40*, 1007.

[5] Fries, S.; Gollnick, K. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 831.

[6] Williams, J. K.; Wiley, D. W.; McKusick, B. C. *J. Am. Chem. Soc.* **1962**, *84*, 2210.



three nitrile bonds are 1.124 (10), 1.131 (14), and 1.126 (12) Å. A marked dissimilarity exists in the lengths of the two carbon–sulfur bonds, 1.742 (S1–C5) vs. 1.698 (S1–C2) Å, and the two α–β carbon–carbon bonds, 1.429 (C4–C5) vs. 1.363 (C2–C3) Å. For reference, the bond lengths in thiophene are C–S, 1.714 Å; C_α–C_β, 1.370 Å; C_β–C_β, 1.423 Å.[7] The distortion of the thiophene ring in **2** probably originates in the delocalization of the lone pair of electrons on the amino group as indicated by resonance structure **3**. The sulfur lone-pair electrons are conjugated with the nitrile group at C-β. The ^{13}C NMR spectrum of **2** also indicates the electron delocalization shown in **3**. The highest field absorption observed is at δ 65.4 (in Me$_2$SO-d_6) and is assigned to the negatively charged carbon in **3**. The



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absorption of the corresponding carbon atom in 2-(2,2-dicyanovinyl)-5-morpholinothiophene is at δ 59.6[8] and the absorption of the β-vinyl carbon atom in [p-(dimethylamino)benzylidene]malonitrile is at δ 71.[9] The ^{1}H NMR spectrum of **2** in acetone-d_6 did not reveal the exchangeable amino protons which, however, did appear in Me$_2$SO-d_6 at δ 7.77. The other absorptions in the ^{13}C and ^{1}H NMR spectra of **2** are similar to those of model compounds, 2-(2,2-dicyanovinyl)thiophene,[8,10] 3-cyanothiophene,[11] and 3-aminothiophene.[12]

A solvent effect analogous to that reported in the thermolysis of 3-vinyl-1,1,2,2-tetracyanocyclobutanes[1] was observed when the decomposition of **1** was attempted in refluxing acetonitrile (bp 82 °C) instead of in refluxing benzene (bp 80 °C). The main product was a black tar along with only a small amount of rearranged product **2**. Within the first hour the solution had become deep purple, indicative of the formation of a charge-transfer complex between thiete and TCNE generated in a cycloreversion.[13] Even at room temperature, a solution of **1** in acetonitrile or acetone slowly becomes violet and a new band at 524 nm appears in the UV–vis spectrum. The cycloreversion in polar solvents probably occurs via a zwitterionic intermediate as has been suggested for both the formation and decomposition of other cycloadducts of TCNE.[5,14]

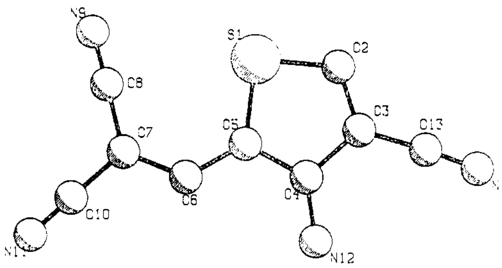
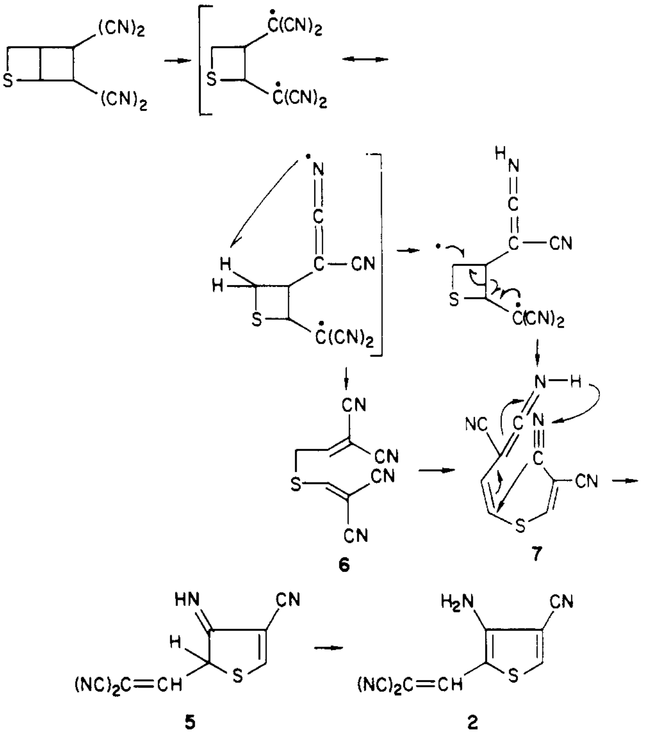
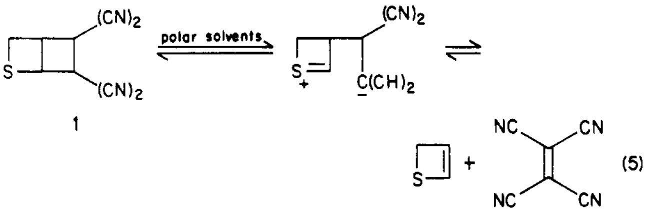


Figure 1. Computer-generated perspective drawing of the final X-ray model of 3-amino-4-cyano-2-(2,2-dicyanovinyl)thiophene. Hydrogens are omitted for clarity.

Scheme I



Since 2H-thiete is thermally unstable,[15] the tarry material probably is formed by its decomposition. To intercept possible dienophilic intermediates, anthracene was added to the reactions of **1** in both acetonitrile and benzene (eq 5). In acetonitrile, a 34% yield of the TCNE adduct with



anthracene was obtained along with 9% of **2** and a red gum probably derived from the decomposition of thiete. The effect of anthracene on the reaction in benzene was null, a 97% yield of **2** being obtained.

In the nonpolar solvent benzene, a different path is followed. No violet color indicative of charge-transfer complexes is seen, and the product **2** is probably formed

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(7) Bak, B.; Christensen, L. H.-N.; Rastrup-Andersen, J. *J. Mol. Spectrosc.* **1961**, *7*, 58.

(8) De, A.; Bhattacharyya, S. P.; Brunskill, J. S. A.; Sidhu, K.; Ewing, D. F. *J. Chem. Res., Suppl.* **1982**, 312.

(9) Posner, T. B.; Hall, D. C. *J. Chem. Soc., Perkin Trans. 2* **1976**, 729.

(10) Musumarra, G.; Ballistreri, F. P. *Chem. Scr.* **1981**, *18*, 209.

(11) (a) Gronowitz, S.; Johnson, I.; Hornfeldt, A.-B. *Chem. Scr.* **1975**, *7*, 76, 111. (b) Terui, Y.; Yamakawa, M.; Honma, T.; Tada, Y.; Tori, K. *Heterocycles* **1982**, *19*, 221.

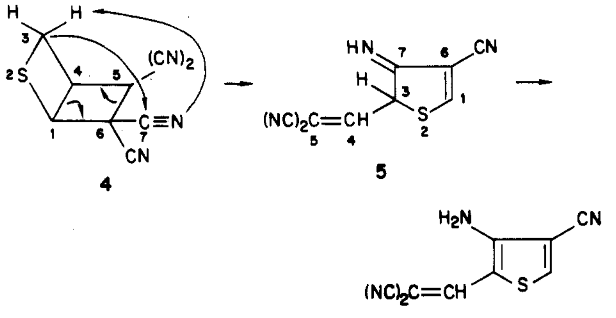
(12) (a) Brunett, E. W.; Altwien, D. M.; McCarthy, W. C. *J. Heterocycl. Chem.* **1973**, *10*, 1067. (b) Rault, S.; de Sevricourt, M. C.; Robba, M. *Recl. Trav. Chim. Pays-Bas* **1982**, *101*, 205.

(13) Methyl vinyl sulfide, an open-chain analogue of thiete, forms a colored complex with TCNE in methylene chloride: Okuyama, T.; Nakada, M.; Toyoshima, K.; Fueno, T. *J. Org. Chem.* **1978**, *43*, 4546.

(14) (a) le Noble, W. J.; Mukhtar, R. *J. Am. Chem. Soc.* **1975**, *97*, 5938. (b) Graf, H.; Huisgen, R. *J. Org. Chem.* **1979**, *44*, 2594. (c) Huisgen, R.; Graf, H. *J. Org. Chem.* **1979**, *44*, 2595.

(15) (a) Dittmer, D. C.; Takahashi, K.; Davis, F. A. *Tetrahedron Lett.* **1967**, 4061. (b) Dittmer, D. C.; Chang, P. L.-F.; Davis, F. A.; Iwanami, M.; Stamos, I. K.; Takahashi, K. *J. Org. Chem.* **1972**, *37*, 1111.

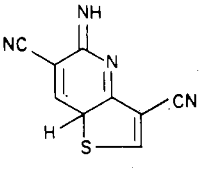
via nonionic intermediates. The transformation of **1** to **2** may proceed via the iminodihydrothiophene **5** whose formation is schematically shown in **4**. Tautomerization of **5** gives **2** (eq 6).



4 **5** **2** (6)

It is unlikely that the events indicated in **4** are concerted, given that the thermal dismutation of a cyclobutane ring to two ethylene moieties is not allowed by Woodward–Hoffmann rules. The rearrangement probably proceeds by a stepwise process analogous to other thermal ring openings of 1,1,2,2-tetracyanocyclobutanes in nonpolar solvents.[1,2] A possible mechanism is given in Scheme I. Zwitteronic intermediates, although possible, are unlikely because of the solvent effect noted above. Although the addition of the inhibitor, hydroquinone, had no effect, the stable dicyanoalkyl radicals shown in Scheme I and postulated in other work[1] may not be efficiently trapped or their lifetime may be short because of the rapidity of the following steps, one of which involves breaking a strained cyclobutane ring with formation of two carbon–carbon double bonds. Ring opening of the initially formed diradical to **6** may precede the 1,5-hydrogen transfer from the methylene group to nitrogen.

The formation of the five-membered ring from intermediate **7**, according to the cyclic process formalized by the arrows shown with **7** in Scheme I, would be allowed by orbital symmetry with antarafacial utilization of the nitrile function: the orbital phase relationships in the HOMO of the linear 11-atom 12-electron system of **7** are appropriate for that hydrogen transfer and the cyclization reaction.[16] Molecular models (CPK) show (for a helical transition state) that the hydrogen atom to be transferred in **7** is positioned conveniently for an antarafacial transfer and that the two carbon atoms to be joined are in close proximity. The basic imino group in **5** may catalyze the tautomerization to **2**. Alternatively, a $4_\pi + 2_\pi$ adduct, **8**, derived from **7**, could yield **5** by a proton shift and a bond scission.[17]



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Experimental Section

Elemental analyses were performed at Microanalysis, Inc., Wilmington, DE. ^{1}H and ^{13}C NMR spectra were recorded on either a Varian T60, Bruker WM-360, or a Mohawk 250 spectrometer. Chemical shifts are reported in ppm downfield from Me$_4$Si. Coupling constants are believed to be accurate to within ±0.2 Hz. Infrared absorption spectra were recorded on a Cary 219 or Cary 118 spectrometer. Mass spectra were obtained on a Finnigan 4000 GC/MS mass spectrometer data system (electron impact). Melting points were recorded on a Mel-Temp apparatus and are uncorrected. Hexane was washed successively with sulfuric acid, water, saturated aqueous sodium bicarbonate, and water, dried (MgSO$_4$), and distilled from Linde molecular sieves, type 4A. Ether was dried and distilled from calcium hydride. Dimethylformamide (DMF) was dried and distilled from calcium hydride, under vacuum, stored over 4A Linde molecular sieves, and protected from light. Benzene was dried and distilled from sodium under nitrogen and stored over 4A molecular sieves. Acetonitrile and methylene chloride were dried over 4A molecular sieves.

5,5,6,6-Tetracyano-2-thiabicyclo[2.2.0]hexane (1). An ether solution of 2*H*-thiete was prepared from trimethyl(3-thietanyl)ammonium iodide (3.0 g, 11.6 mmol).[15] Tetracyanoethylene (1.48 g, 11.6 mmol) in dry methylene chloride (150 mL) was added to the thiete solution with stirring at room temperature. After 2 h a white solid had precipitated. The reaction mixture was stirred for an additional 24 h after which the precipitate was removed by filtration (1.28 g, 6.40 mmol, 55% based on the quaternary ammonium salt): mp 137 °C [becomes purple, 143–144 °C (dec to a dark purple melt)]; ^{1}H NMR (360 MHz, acetone-d_6) δ 3.47 (doublet of triplets, J = 1.5, 1.7, 11.5 Hz, 1 H), 4.08 (dd, J = 7.8, 11.5 Hz, 1 H), 4.61 (septet, J = 1.7, 6.0, 7.7 Hz, 1 H), 4.82 (dd, J = 1.5, 6.1 Hz, 1 H); ^{13}C NMR (acetone-d_6) δ 28.1 (dd), 42.8 (s), 47.1 (s), 47.4 (d), 49.6 (d), 110.9 (s), 111.4 (s), 112.0 (s), 112.4 (s); IR (KBr) 2250 (CN, m) cm^{-1}; UV (CH$_3$CN) 432 (ϵ 170), 260 nm (ϵ 158); MS, m/e (relative intensity) 200 (M, 6.7), 91 (M − SCHC(CN)$_2$, 31), 72 (M − C$_6$N$_4$, 100). A pure sample was obtained by recrystallization from methylene chloride–ether. Anal. Calcd for C$_9$H$_4$N$_4$S: C, 53.99; H, 2.01. Found: C, 54.24; H, 2.07.

In a similar manner, adduct **1** was prepared from 2*H*-thiete obtained by dehydrohalogenation of 3-chlorothietane. Potassium *tert*-butoxide (6.0 g, 53 mmol) in dry DMF (75 mL) was added under nitrogen during 30 min to a cold (−20 °C) solution of 3-chlorothietane[19] (3.8 g, 35 mmol) in dry DMF (10 mL). The reaction mixture was stirred and cooled in a dry ice–acetone bath. The reaction mixture became dark and viscous on addition of the potassium *tert*-butoxide. After the addition was completed, the reaction mixture was warmed to −10 °C and stirred for 30 min. (It is very important that the internal temperature of the reaction mixture be monitored at all times and that good stirring be maintained.) Glacial acetic acid (4 mL) was added to the mixture which was distilled under vacuum (2 mm) through traps cooled to −78 °C and −25 °C in dry ice–acetone baths. The reaction mixture was warmed to 30 °C during the distillation. A concentrated solution of 2*H*-thiete in a small amount of DMF and *tert*-butyl alcohol were present in the −78 °C trap. The −25 °C trap contained a dilute solution of thiete in DMF. The ^{1}H NMR spectrum and formation of a 2,4-nitrophenylhydrazone[15b] indicated approximately 0.650 g (9.0 mmol, 26%) of 2*H*-thiete in the −78 °C trap: ^{1}H NMR (neat) δ 3.80 (d, 2 H), 5.60 (dt, 1 H), 6.46 (d, 1 H) (identical with the ^{1}H NMR spectrum previously reported).[15b] The yield of TCNE adduct was 24% based on 3-chlorothietane.

3-Amino-4-cyano-2-(2,2-dicyanovinyl)thiophene · (2). 5,5,6,6-Tetracyano-2-thiabicyclo[2.2.0]hexane (**1**) (0.146 g, 0.730 mmol) in benzene (50 mL) was refluxed for 24 h. A yellow solid

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[16] Streitwieser, A., Jr.; Braumann, J. I. "Supplemental Tables of Molecular Orbital Calculations"; Pergamon: Oxford, 1965; Vol. 1, pp 66–67. HMO calculations on the heteratom system 7 indicate somewhat larger overlap for the two carbon atoms being joined than the calculations reported by Streitwieser and Braumann for the decapentaene system.

[17] We are indebted to a referee for this suggestion.

[18] All crystallographic calculations were done on a PRIME 850 computer operated by the Cornell Chemistry Computing Facility. Principal programs employed were REDUCE and UNIQUE, data reduction programs by M. E. Leonowicz, Cornell University, 1978; MULTAN78, a system of computer programs for the automatic solution of crystal structures from X-ray diffraction data (locally modified to perform all Fourier calculations including Patterson syntheses) written by P. Main, S. E. Hull, L. Lessinger, G. Germain, J. P. Declercq, and M. M. Woolfson, University of York, England, 1978; BLS78A, an anisotropic block-diagonal least-squares refinement written by K. Hirotsu and E. Arnold, Cornell University, 1980; PLUTO78, a crystallographic illustration program by W. D. S. Motherwell, Cambridge Crystallographic Data Centre, 1978; and BOND, a program to calculate molecular parameters and prepare tables written by K. Hirotsu, Cornell University, 1978.

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precipitated during refluxing (0.140 g, 0.700 mmol, 96%): mp 239–240 °C; ^1H NMR (acetone-d_6) δ 8.30 (s, 1 H), 8.67 (s, 1 H); ^1H NMR (Me_2SO-d_6) δ 7.77 (s, 2 H), 8.50 (s, 1 H), 8.87 (s, 1 H); ^{13}C NMR (acetone-d_6) δ 157.6, 148.1, 147.2, 116.1, 115.3, 113.1, 109.0, 103.3, 69.7; ^{13}C NMR (Me_2SO-d_6) δ 157.7 (s), 148.9 (d), 147.8 (d), 116.0 (s), 115.1 (s) 112.8 (s), 107.2 (s), 101.6 (s), 65.4 (s); IR (KBr) 3400 (NH_2, m), 3360 (NH_2, m), 3250 (NH_2, m), 3120 (w), 2215 (CN, s), 1670 (s), 1630 (w), 1565 (s) cm^{-1}; UV (CH_3CN) 408 (ϵ 27 500), 330 (7700), 320 (7400), 228 (22 900) nm; MS, *m/e* (relative intensity) 200 (M, 100), 173 (M – HCN, 94), 146 (M – C_3H_4N, 12.4), 121 (M – $C_4H_3N_2$, 11), 94 (M – $C_5H_4N_3$, 24). A pure sample was obtained by recrystallization from acetonitrile. Anal. Calcd for $C_9H_4N_4S$: C, 53.99; H, 2.01; N, 27.98; S, 16.01. Found: C, 53.79; H, 2.10; N, 27.84; S, 16.26.

Single-Crystal X-ray Diffraction Analysis of 2. Crystals of 2 suitable for X-ray diffraction could be grown from acetonitrile or methanol solutions by slow evaporation of the solvent. The crystal used in the determination was grown from methanol. Preliminary X-ray photographs displayed only triclinic symmetry, and accurate lattice constants of a = 12.205 (6) Å, b = 14.018 (5) Å, c = 3.836 (2) Å, α = 94.61 (3)°, β = 81.76 (4)°, and γ = 118.12 (3)° were determined from a least-squares fit of 15 moderate 2θ values. Density considerations indicated two molecules of composition $C_9H_4N_4S$ in the unit cell. Space group $P\bar{1}$ was assumed, and this was verified by successful refinement. All unique diffraction maxima with $2\theta \leq 114°$ were collected on a computer-controlled four-circle diffractometer using a variable speed 1° ω scan and graphite-monochromated Cu K$\bar{\alpha}$ radiation (1.54178 Å). Of the 1575 reflections surveyed in this manner, 1050 (67%) were judged observed after correction for Lorentz, polarization, and background effects ($|F_o| \geq 3\sigma(F_o)$).[18] A phasing model was found by standard heavy atom techniques after the sulfur position was deduced from the Patterson synthesis. Hydrogen atoms and a methanol of crystallization were found in a difference electron density synthesis after partial refinement of the heavy atom positions. The current model has anisotropic heavy atoms and isotropic hydrogens and has been refined to a standard crystallographic residual of 0.070 for the observed reflections. Additional crystallographic parameters are available. Please consult the paragraph headed Supplementary Material Available for details.

Treatment of 5,5,6,6-Tetracyano-2-thiabicyclo[2.2.0]hexane with Anthracene in Refluxing Acetonitrile. 5,5,6,6-Tetracyano-2-thiabicyclo[2.2.0] hexane (1) (0.137 g, 0.685 mmol) and anthracene (0.178 g, 1.00 mmol) in acetonitrile (10 mL) were refluxed for 12 h. The color of the solution changed from pale yellow to violet after refluxing. When the solution was cooled, anthracene (0.030 g, 0.168 mmol) precipitated. The solvent was removed and methylene chloride (50 mL) was added to give a yellow precipitate (0.012 g, 0.060 mmol, 9%) that was identified as 2 from its mp, IR spectrum, and TLC behavior in comparison with authentic material. Removal of the solvent gave a brown solid (0.225 g) which was a mixture of at least three substances as indicated by thin-layer chromatography (methylene chloride/hexane, 1:1, silica gel): anthracene; 9,10-dihydro-9,10-ethanoanthracene-11,11,12,12-tetracarbonitrile, and a polar material at the origin. Column chromatography (methylene chloride/hexane, 1:1, silica gel, 100 g) was used to partially separate a mixture of anthracene and anthracene–TCNE adduct from the polar material. Anthracene and its TCNE adduct were then further separated by preparative TLC (methylene chloride/hexane, 1:1, silica gel): anthracene (0.10 g, 0.56 mmol); 9,10-dihydro-9,10-ethanoanthracene-11,11,12,12-tetracarbonitrile (0.072 g, 0.23 mmol, 34%). The spectroscopic properties and the melting point behavior [mp 264–268 °C dec; lit.[20] mp 268–270 °C dec] of the anthracene–TCNE adduct were identical with those of the authentic compound (mp 264–268 °C) that was synthesized independently from anthracene and tetracyanoethylene.[20] The polar material was removed from the column by elution with acetonitrile. Removal of the solvent gave a red, sticky solid (0.053 g).

Treatment of 5,5,6,6-Tetracyano-2-thiabicyclo[2.2.0]hexane with Anthracene in Refluxing Benzene. A mixture of 5,5,6,6-tetracyano-2-thiabicyclo[2.2.0]hexane (0.096 g, 0.480 mmol), anthracene (0.089 g, 0.500 mmol), and benzene (10 mL) was refluxed for 12 h. 3-Amino-4-cyano-2-(2,2-dicyanovinyl)thiophene (0.093 g, 0.465 mmol, 97%) precipitated during refluxing and was isolated by filtration and identified by its spectroscopic properties in comparison with those of the authentic compound. The anthracene was quantitatively recovered from the benzene filtrate.

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Registry No. 1, 94732-90-8; 2, 94732-91-9; 2*H*-thiete, 503-31-1; tetracyanoethylene, 670-54-2; 3-chlorothietane, 6013-95-2; anthracene, 120-12-7; 9,10-dihydro-9,10-ethanoanthracene-11,11,12,12-tetracarbonitrile, 1625-84-9.

Supplementary Material Available: Tables of fractional coordinates, thermal parameters, bond distances, and bond angles for compound 2 (4 pages). Ordering information is given on any current masthead page.

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C-Alkylation and N-Acylation of 4-Amino-1-azabutadiene Derivatives. A Convenient Route to Monoalkylated 1,3-Diketones

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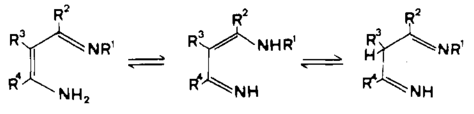
Alkylation of 4-amino-1-azabutadiene derivatives 1 with different alkyl halides followed by acid hydrolysis gives mono-C-alkylated 1,3-diketones 3 in excellent yields. In contrast acylation of 1 occurs at the imine nitrogen.

4-Amino-1-azabutadiene derivatives, 1, are suitable starting materials for the synthesis of five- and six-membered heterocycles.[1]

Compounds 1 are easily obtained by reaction of Schiff bases with saturated nitriles in the presence of $AlCl_3$.[2]

Scheme I



1

Thus, 4-amino-1-azabutadienes 1 are prepared under mild conditions and high yields when R^3 = H, CH_3. The system

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(1) (a) Barluenga, J.; Jardón, J.; Rubio, V.; Gotor, V. *J. Org. Chem.* **1983**, *48*, 1379. (b) Barluenga, J.; Rubio, V.; Gotor, V. *J. Org. Chem.* **1980**, *45*, 2592.

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