The high positional selectivity inherent in the reaction of **1** and **2** with monosubstituted aromatics is partially attributable to steric interactions between the bulky attacking electrophile and a substituent in the ortho position. However, in agreement with the results of Olah and Schilling,[4] high para selectivity can also be attributed to formation of a thermodynamically more stable para σ complex under superacid conditions, particularly at the low temperatures involved.

The fact that CS_2 is often used as a solvent in Friedel–Crafts reactions raises the question whether it is alkylated by RX/AlX_3 to form a species like **1a**. To our knowledge, however, the formation of dithioesters as a side reaction in Friedel–Crafts alkylation has not been reported.[12]

Experimental Section

All staring materials were commercially available. Antimony pentafluoride (Cationics, Inc.) was doubly distilled in glass under an inert atmosphere before use. Ethyl fluoride (PCR), methyl fluoride (Matheson), and ethylene (Airco) were used as received. Carbonyl sulfide (Matheson) was purified through a drying train of calcium chloride, calcium sulfate, and mercuric oxide. Carbon disulfide (Mallinckrodt) was stored over molecular sieves.

Infrared and ^1H NMR spectra were recorded on Perkin-Elmer Model 297 and Varian Associates Model A56-60 spectrometers, respectively. Tetramethylsilane was used as an external standard. Thin-layer chromatography was performed on silica gel plates with hexane as eluent.

The general procedure for the carboxylation of aromatics with **1** or **2** in SO_2 was as follows. A solution of the alkylating agent was prepared by introducing a slight excess of alkyl fluoride into a solution of antimony pentafluoride (10.0 mmol) in SO_2 (15 mL) at −78 °C. Excess carbon disulfide or carbonyl sulfide was then added to this vigorously stirred solution, and in the case of methyl fluoride-antimony pentafluoride, the solution temperature was allowed to rise to −30 °C for 15 min to ensure complete formation of **2a**. Ethylation with ethyl fluoride–antimony pentafluoride of **1b** or **2b** was instantaneous at −60 °C. The progress of the reaction is indicated by the disappearance of the upper layer of CS_2 as **1a** is formed.

The aromatic substrate (10 mmol) was then dissolved in 5 mL of SO_2, cooled to the reaction temperature, and added dropwise to the well-stirred, light yellow solution of the carboxylating agent. After being stirred for the specified time, the reaction mixture was poured over ice, extracted three times with 100-mL portions of 10% $NaHCO_3$ solution and distilled water, respectively, and dried over anhydrous $MgSO_4$. After removal of pentane from the product by rotary evaporation, the pure ester was obtained by vacuum distillation or recrystallization. The compounds obtained gave satisfactory elemental analysis (Galbraith Laboratories).

Acknowledgment. Support of our work by the National Institutes of Health and the National Science Foundation is gratefully acknowledged. F.L.C. thanks CNRS and the Institute of Macromolecular Chemistry of the Louis Pasteur University, Strasbourg, for support and a fellowship.

Registry No. 1a, 75599-66-5; **1b**, 75599-68-7; **2a**, 75626-81-2; **2b**, 75599-70-1; methyl benzenedithiocarboxylate, 2168-78-7; methyl toluenedithiocarboxylate, 75599-50-7; methyl *o*-xylenedithiocarboxylate, 75599-51-8; methyl *m*-xylenedithiocarboxylate, 75599-52-9; methyl *p*-xylenedithiocarboxylate, 75599-71-2; methyl anisoledithiocarboxylate, 75626-80-1; methyl cumenedithiocarboxylate, 75599-53-0; methyl mesitylenedithiocarboxylate, 58863-45-9; methyl fluorobenzenedithiocarboxylate, 75599-54-1; methyl benzenethiocarboxylate, 5925-68-8; methyl toluenethiocarboxylate, 75599-55-2; methyl *o*-xylenethiocarboxylate, 75599-56-3; methyl *m*-xylenethiocarboxylate, 75599-57-4; methyl anisolethiocarboxylate, 75599-58-5; methyl cumenethiocarboxylate, 75599-59-6; methyl mesitylenethiocarboxylate, 39248-77-6; methyl fluorobenzenethiocarboxylate, 75599-60-9; methyl chlorobenzenethiocarboxylate, 75599-61-0; methyl bromobenzenethiocarboxylate, 75599-62-1; polystyrene, 9003-53-6; ethyl benzenethiocarboxylate, 1484-17-9; ethyl toluenethiocarboxylate, 75599-63-2; ethyl anisolethiocarboxylate, 75599-64-3; ethyl *m*-xylenethiocarboxylate, 75599-65-4; ethyl ethylbenzenethiocarboxylate, 75599-72-3; CS_2, 75-15-0; COS, 463-58-1.

(12) G. A. Olah, "Friedel–Crafts and Related Reaction", Vol. 3, Wiley-Interscience, New York, 1964, Part 2, Chapter 39.

Notes

Syntheses of Seven-Membered Cyclic Azo Compounds[1]

C. G. Overberger*[2] and Timothy F. Merkel[3]

Department of Chemistry, The University of Michigan, Ann Arbor, Michigan 48109

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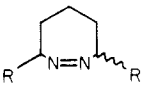
The chemistry of both cyclic and acyclic azo compounds has been investigated extensively in our laboratory since 1949.[1] Attention has been focused recently on the study of seven- to ten-membered-ring systems. Previous thermal and photochemical decomposition studies of medium-sized cyclic azo compounds in solution and in the solid state have provided interesting data on the stereoselectivity of product formation observed in these reactions and the characteristics of the radical intermediates that were produced during decomposition.

In conjunction with this research effort, we report the synthesis of the seven-membered cyclic azo compounds of this series. The compounds 1,2-diaza-(*Z*)-1-cycloheptene (**1**) and *cis*- and *trans*-3,7-dimethyl-1,2-diaza-(*Z*)-1-cycloheptenes (**2** and **3**, respectively) have been synthesized and characterized. The synthesis of *cis*-3,7-diphenyl-1,2-diaza-(*Z*)-1-cycloheptene (**4**) has been reported previously.[4,5]



1, R = H
2, R = CH_3 (cis)
3, R = CH_3 (trans)
4, R = C_6H_5 (cis)

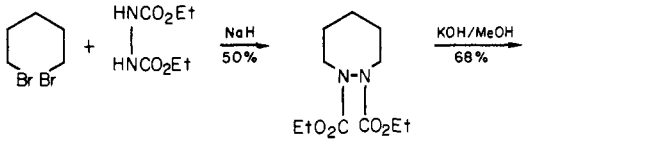
(1) This is the 53rd in a series of papers concerned with the preparation and decomposition of azo compounds. For the previous paper see C. G. Overberger and Minn-Shong Chi, *J. Org. Chem.*, companion paper in this issue.
(2) Author to whom correspondence may be addressed.
(3) Taken in part from the Ph.D. Thesis of T. F. Merkel, The University of Michigan, 1973.

0022-3263/81/1946-0442$01.00/0

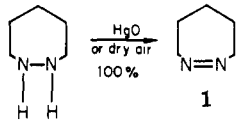
Results and Discussion

1. Syntheses. The general synthetic approach to the seven-membered cyclic azo compounds involved the condensation of the appropriate dibromide or ditosylate with 1,2-dicarbethoxyhydrazine, hydrolysis of the resulting diester, and decarboxylation to form the hydrazine, with subsequent oxidation to the desired azo compound. This procedure is similar to that utilized by Overberger and Stoddard[6] for the preparation of eight-membered cyclic azo compounds.

Thus, the initial step in the preparation of the unsubstituted compound 1,2-diaza-(*Z*)-1-cycloheptene (**1**) was condensation under prolonged heating of 1,2-dicarbethoxyhydrazine with 1,5-dibromopentane using sodium hydride as the base to yield 1,2-dicarbethoxy-1,2-diazacycloheptane (**5**). The NMR spectrum of compound **5**



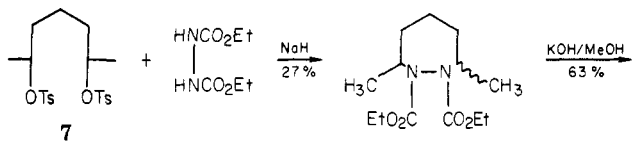
5



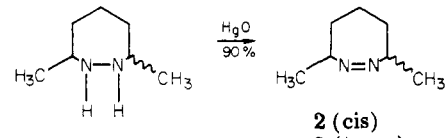
6 **1**

displayed two sets of magnetically nonequivalent α-methylene protons. Removal of the carbethoxy groups of compound **5** by saponification and decarboxylation with potassium hydroxide in refluxing methanol afforded the cyclic hydrazine **6**,[7] which proved to be extremely sensitive to air oxidation. In the presence of moisture, the azo compound isomerized rapidly to the corresponding hydrazone. Analytically pure 1,2-diazacycloheptane (**6**) could be obtained by vacuum distillation on a spinning-band column under dry nitrogen. Hydrazine **6** was readily oxidized to 1,2-diaza-(*Z*)-1-cycloheptene (**1**), either by dry air or by mercuric oxide.

The preparation of *cis*- and *trans*-3,7-dimethyl-1,2-diaza-(*Z*)-1-cycloheptenes (**2** and **3**) required the condensation of dicarbethoxyhydrazine with the ditosylate of 2,6-heptanediol, itself derived from 2,6-heptanedione[8] by sodium borohydride reduction.[9] The resultant mixture of diesters (**8**) was hydrolyzed and decarboxylated to the dimethyl-substituted cyclic hydrazines, **9** and **10**. These could be subjected without prior separation to oxidation by mercuric oxide to afford a mixture of *cis*- and *trans*-3,7-dimethyl-1,2-diaza-(*Z*)-1-cycloheptenes (**2** and **3**, respectively). Separation of hydrazines **9** and **10** could be effected by repeated distillation through a spinning-band column with a nitrogen bleed. The lower boiling isomer was found to be the trans compound **10** and to be oxidized by mercuric oxide relatively slowly, oxidation requiring 34 h for completion. On the other hand, the *cis*-dimethyl isomer **9** was completely oxidized to *cis*-3,8-dimethyl-1,2-diaza-(*Z*)-1-cycloheptane (**2**) within 18 h.



7 **8**



9 (cis)
10 (trans)

2 (cis)
3 (*trans*)

2. Stereochemical Assignments. The prohibitive steric strain that would be imposed on these seven-membered cyclic azo compounds by a *trans*-azo linkage should ensure the *cis*-azo configuration for compounds **1** through **4**. This expectation is substantiated by dipole moment and ultraviolet data as well as europium shift studies. The relevant data for the title compounds are summarized and compared to previously reported analogous cases in Table I.

Ultraviolet absorption maxima of the *cis*-azo linkage usually appear at wavelengths greater than ~375 nm and exhibit larger extinction coefficients than those of the corresponding *trans*-azo compounds. For instance, 1,2-diaza-(*Z*)-1-cyclooctene (**11**) exhibits an ultraviolet absorption maximum at 389 nm (ϵ 110), whereas its trans isomer, 1,2-diaza-(*E*)-1-cyclooctene (**12**), has an absorption maximum at 372 nm (ϵ 35).[10-12] The ultraviolet data for the seven-membered cyclic azo compounds of this study all support the cis geometry: 1,2-diaza-(*Z*)-1-cycloheptene (**1**) with 393 nm (ϵ 158), *cis*-3,7-dimethyl-1,2-diaza-(*Z*)-1-cycloheptene (**2**) with 396 nm (ϵ 152), *trans*-3,7-dimethyl-1,2-diaza-(*Z*)-1-cycloheptene (**3**) with 401 nm (ϵ 85.5), and *cis*-3,7-diphenyl-1,2-diaza-(*Z*)-1-cycloheptene (**4**) with 390 nm (ϵ 127).

Furthermore, it has been observed[5,10] that *cis*-azo compounds generally have dipole moments larger than 2 D, whereas their trans counterparts display much smaller dipole moments, as is demonstrated by the cis and trans isomers of 1,2-diaza-1-cyclooctene (**11** and **12**) with 3.09 and 1.10 D, respectively. The dipole moments of compounds **1**, **2**, **3**, and **4** have been determined (in that order) as 3.02, 2.97, 2.85, and 2.42, all very well within the range ascribable to cis-linked azo compounds.

NMR europium shift data further confirm the cis configuration for the seven-membered cyclic azo compounds of this study. Since the two pairs of nonbonded electrons are oriented on the same side of a *cis*-azo double bond, coordination with the europium complex $Eu(fod)_3$ is expected to be stronger for the *cis*-azo compounds than for their trans analogues. This has been confirmed experimentally.[10-12] In addition, the stronger coordination of the *cis*-azo group gives rise to a larger upfield shift for the methyl protons of the shift reagent and this may be used as a reference of azo coordination power. The ΔEu values included in Table I are clearly consistent with the *cis*-azo geometry for compounds **1**-**4**.

Experimental Section

All boiling points and melting points were determined with a Thomas-Hoover capillary melting point apparatus and are uncorrected. Infrared spectra were taken on a Perkin-Elmer Model

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(6) C. G. Overberger and J. W. Stoddard, *J. Am. Chem. Soc.*, **92**, 4922 (1970).
(7) G. Zinner and W. Deucker, *Arch. Pharm.*, **295**, 526 (1962).
(8) C. G. Overberger, T. B. Gibb, Jr., S. Chibnik, P.-T. Huang, and J. J. Monagle, *J. Am. Chem. Soc.*, **74**, 3290 (1952).
(9) J. Dale, *J. Chem. Soc.*, 910 (1961).
(10) C. G. Overberger, J.-P. Anselme, and J. R. Hall, *J. Am. Chem. Soc.*, **85**, 2752 (1963).
(11) C. G. Overberger, M.-S. Chi, D. Pucci, and J. A. Barry, *Tetrahedron Lett.*, 4565 (1972).
(12) G. Vitt, E. Hädicke, and G. Quinkert, *Chem. Ber.*, **109**, 518 (1976).

Table I. Spectral Data of Cyclic Azo Compounds

compd	μ, D	UV maxima[a] nm	ε	ΔEu values α-H	Eu(fod)$_3$[b]	ref
1	3.02	393	158	25.0[d]	9.92	this work
11	3.09	389	110	24.0[c]	9.35	1, 10-12
1,2-diaza-(*E*)-1-cyclooctene	1.10	372	35	7.5 (H_B)[e] 9.0 (H_A)	8.72	1,11
1,2-diaza-(*E*)-1-cyclononene	1.24	371	60	5.5[c]	8.67	1,11
3	2.85	396	152	11.5[d]	9.25	this work
2	2.97	401	85.5	14.3[d]	9.24	this work
4	2.42	390[e]	127	11.7[d]	9.20	4, 5

[a] In isooctane, unless otherwise noted. [b] For the methyl protons of Eu(fod)$_3$ at ratio 0.1. [c] In CCl_4. [d] In $CDCl_3$. [e] In $CHCl_3$.

257 grating infrared spectrophotometer while ultraviolet spectra were measured with a Perkin-Elmer Model 402 ultraviolet-visible spectrophotometer. Nuclear magnetic resonance spectra were recorded on either a Varian Model A-60 or Varian Model T-60 spectrometer, using tetramethylsilane or sodium 2,2-dimethyl-2-silapentane-5-sulfonate as internal standard.

Gas chromatographic analyses were determined on a Varian-Aerograph Model 90P-3 unit equipped with a Varian-Aerograph linear temperature programmer and an F and M Scientific Model 50B automatic attenuator. Mass spectra were obtained by the Department of Chemistry, The University of Michigan, Ann Arbor, MI, while microanalyses and molecular-weight determinations were performed by Spang Microanalytical Laboratories, Eagle Harbor, MI.

Refractive index values were determined on a Bausch and Lomb, Abbe-3L, refractometer.

Synthesis of 1,2-Dicarbethoxy-1,2-diazacycloheptane (5). To a slurry of 25.2 g (0.596 mol) of sodium hydride (57% mineral oil dispersion which was washed with three 25–30-mL portions of benzene or hexane previously dried over molecular sieves) in 400 mL of dry diglyme was added 42.0 g (0.238 mol) of solid 1,2-dicarbethoxyhydrazine. The solid's addition funnel was rinsed with 150 mL of diglyme.

The mixture was heated to approximately 70 °C for 1 h to allow cessation of hydrogen evolution before 54.8 g (0.238 mol) of 1,5-dibromopentane was added dropwise over 50 min followed by a 50-mL diglyme wash. The temperature was raised gradually to 130–135 °C. After 10 h, the temperature was increased to reflux (~155–160 °C) for an additional 72 h. The mixture was allowed to cool to room temperature with stirring overnight.

The solids were removed by suction filtration through a bed of Celite, 150 mL of water was added, and the solution was extracted with four 500-mL portions of ether and two 250-mL portions of chloroform. The combined organic layers were dried over anhydrous magnesium sulfate, filtered, and concentrated on the rotary evaporator. Two distillations of the residue under high vacuum gave 29.1 g (50%) of the desired diester: colorless, viscous oil; bp 75–77 °C (5 × 10^{-5} mm); n^{25}_D 1.4627; IR (neat) 5.85 μm (C=O); NMR (CCl_4) δ 4.10 (q, 4, OCH_2), 3.80 (d, 2, NCH), 3.10 (d, 2, NCH ax), 1.65 (s, 6, CH_2), 1.20 (t, 6, CH_3). Anal. Calcd for $C_{11}H_{20}N_2O_4$: C, 54.08; H, 8.25; N, 11.47. Found: C, 54.14; H, 8.31; N, 11.43.

Synthesis of 1,2-Diazacycloheptane (6). A solution of 46.4 g (0.827 mol) of potassium hydroxide in 196 mL of absolute methanol was added to 36.0 g (0.147 mol) of 1,2-dicarbethoxy-1,2-diazacycloheptane (5). The mixture was heated at reflux for 24 h with constant agitation (magnetic stirring bar). An additional 30.8 g (0.549 mol) of potassium hydroxide was added in pellet form and the mixture allowed to reflux for 72 h more.

After the mixture cooled to room temperature, the solids were removed by filtration and washed with a small amount of ether. Excess methanol was removed on the rotary evaporator under N_2 at a maximum bath temperature of 30 °C before 400 mL of distilled water was added and the solution was subjected to continuous ether extraction for 3 days, again under a blanket of N_2. At the end of the extraction period, the water layer contained in the collection flask was separated from the ether layer and extracted with two 125-mL portions of $CHCl_3$. The combined organic layers were dried twice under N_2, using an anhydrous mixture of $MgSO_4$ and K_2CO_3. After filtration, the solvents were removed on the rotary evaporator at room temperature under N_2. Two distillations under N_2 through a short-path distillation apparatus afforded 10.0 g (68% yield) of the light yellow 1,2-diazacycloheptane (6): bp 57 °C (17 mm); n^{22}_D 1.4860; IR (neat) 3.02 μm (NH); NMR ($CDCl_3$) δ 3.20 (s, 2, NH), 2.85 (m, 4, N-CH_2), 1.65 (m, 6, CH_2).

Since this compound was extremely unstable to air oxidation, it was characterized as the monooxalic and the monotartaric acid salt.

Synthesis of the Monooxalic Acid Salt of 1,2-Diazacycloheptane. To a rapidly stirred solution of 3.78 g (0.03 mol) of oxalic acid in 60 mL of distilled water was added dropwise 3.00 g (0.030 mol) of 1,2-diazacycloheptane at 75 °C. The temperature was gradually increased to 91 °C and the solution was held at 91 °C for 0.5 h, cooled to room temperature, and extracted with four 60-mL portions of ether and three 60-mL portions of $CHCl_3$. The aqueous layer was evaporated on the rotary evaporator and the solids were dissolved in a minimum amount of warm, distilled water. After filtration of the warm solution, the product was crystallized, filtered, and washed with small amounts of chloroform and ether to yield 3.72 g of white needles (65%), mp 164–165 °C, dec with gas evolution. Recrystallization from EtOH/H_2O (2.4:1 volume ratio) increased the melting point of the fine, white needles to 170–171 °C, dec with gas evolution: IR (KBr) 3.08 (NH), 5.8 (C=O), 6.27 μm (COO^-); NMR (D_2O) δ 4.70 (s, NH, COOH exchanging with D_2O), 3.20 (m, 4, NCH_2), 1.75 (s, 6, CH_2). Anal. Calcd for $C_7H_{14}N_2O_4$: C, 44.20; H, 7.42; N, 14.73. Found: C, 44.16; H, 7.32; N, 14.63.

Synthesis of the Monotartaric Acid Salt of 1,2-Diazacycloheptane. To a magnetically stirred solution of 0.750 g (5 × 10^{-3} mol) of *d*-(+)-tartaric acid in 10 mL of distilled water was added dropwise 0.500 g (5 × 10^{-3} mol) of 1,2-diazacycloheptane (7) at room temperature. The mixture was agitated for 0.5 h and was then extracted with 120 mL of ether (3 × 40 mL) and 80 mL of chloroform (2 × 40 mL). After removal of the water from aqueous layer on the rotary evaporator, the remaining light yellow oil was crystallized twice from a minimum amount of warm absolute EtOH. The solids were dried under high vacuum at room temperature, yielding 0.78 g (62.4%) of off-white crystals: mp 108.5–110.5 °C; IR (KBr) 3.07 (OH), 3.12 (NH), 5.81 (C=O), 6.39 μm (COO^-); NMR (D_2O) δ 4.60 (s, average for HOD, CHOH, NH, and COOH), 4.40 (s, 2, CHOH), 3.10 (m, 4, NCH_2), 1.70 (s, 6, CH_2). Anal. Calcd for $C_9H_{18}N_2O_6$: C, 43.19; H, 7.25; N, 11.20. Found: C, 43.26; H, 7.18; N, 11.26.

Synthesis of 1,2-Diaza-(*Z*)-1-cycloheptene. Analytically pure 1,2-diaza-1-cycloheptene (1) could only be obtained by oxidation of analytically pure 1,2-diazacycloheptane (6) which had been freshly distilled under nitrogen. After preliminary purification by two distillations through a short-path distillation head, the hydrazine was purified by distillation at aspirator pressure through a Nester–Faust annular Teflon spinning-band column equipped with an automatic control console. Two passes through the column were necessary to obtain pure hydrazine. Typical of the column conditions needed to effect the distillation was a reflux ratio of 200:1 with a reflux drop rate of 6 to 10 drops per minute. A temperature gradient of 5 to 10 degrees over the length of the column was also necessary.

(a) Oxidation by Dry Air. A solution of 0.250 g (2.5 × 10^{-3} mol) of 1,2-diazacycloheptane (6) in 2.5 mL of dry benzene was stirred magnetically for 48 h. The yellow solution was diluted

with fresh benzene, dried over anhydrous $MgSO_4$, filtered, and evaporated on the rotary evaporator, all under N_2. Lyophilization removed the final traces of solvent to yield a nearly quantitative amount of the pure 1,2-diaza-(*Z*)-1-cycloheptene (1). Compound 1 is a pale yellow oil: bp 57 °C (17 mm); n^{24}_D 1.4850; IR (neat) 6.4 μm (N=N); UV (isooctane) λ_{max} 393 nm (ε 158); NMR ($CDCl_3$) δ 4.30 (t, 4, NCH_2), 1.60 (m, 6, CH_2). Anal. Calcd for $C_5H_{10}N_2$: C, 61.18; H, 10.27; N, 28.55. Found: C, 61.36; H, 10.26; N, 28.37.

(b) Oxidation by Mercuric Oxide. A mixture of 28.4 g (0.284 mol) of 1,2-diazacycloheptane (6), 491 mL of dry tetrahydrofuran, 2 g of anhydrous magnesium sulfate, and 246 g (1.14 mol) of HgO was stirred magnetically under N_2 for 24 h. The HgO was then removed by filtration through Celite. Evaporation of the solvent under N_2, lyophilization, and a pot-to-pot distillation under high vacuum at room temperature afforded the 1,2-diaza-(*Z*)-1-cycloheptene (1) in better than 95% yield.

Synthesis of 2,6-Heptanediol. The method used was adapted from the work of Dale[9] who reported the reduction of acetylacetone.

A solution of 2.95 g (0.0781 mol) of sodium borohydride and 0.059 g (0.001 47 mol) of NaOH in 30 mL of distilled water was cooled in an ice bath. To this stirred solution was added dropwise 16.0 g (0.125 mol) of 2,6-heptanedione[8] dissolved in 30 mL of absolute MeOH during 1 h at 10 to 15 °C. After the addition was complete, the ice bath was removed and the liquid was agitated overnight at room temperature.

Excess MeOH was removed and the remaining solution was extracted with 320 mL of ether (4 × 80 mL). The ether extracts were dried over anhydrous $MgSO_4$, filtered, and evaporated to yield 16.3 g (98.8%) of 2,6-heptanediol. The compound was shown to be analytically pure by GLC analysis.

The diol is a colorless, viscous liquid: bp 75–77 °C (0.2 mm); IR (neat) 3.02 μm (OH); NMR ($CDCl_3$) δ 3.70 (m, 2, CH), 3.40 (s, 2, OH), 1.40 (s, 6, CH_2), 1.10 (d, 6, CH_3).

Synthesis of 2,6-Heptaneditosylate (7). To a rapidly stirred solution of 42.4 g (0.322 mol) of 2,6-heptanediol in 465 mL of pyridine was added 244 g (1.25 mol) of *p*-toluenesulfonyl chloride in small portions, the temperature being held at 0 to −5 °C. The addition took 45 min. The reaction mixture was then stirred at below 0 °C for 2 h before it was refrigerated overnight.

The reaction mixture was poured over 626 g of crushed ice, and the aqueous solution was extracted with 1800 mL of ether (9 × 200 mL). The combined ether extracts were washed with 1 L of 6 N HCl and dried over $MgSO_4$. Filtration and removal of the solvent afforded 132 g of yellow-brown oil. This material was dissolved in a minimum amount of absolute MeOH and was rapidly stirred while cooling in an ice bath for several hours. Fine white granules were collected by filtration, washed with a minimum amount of cold MeOH, and dried in a vacuum oven at room temperature for 14 h: 115.5 g (82.0%) of white solid; mp 55–57 °C; IR (KBr) 11.2, 7.4, 8.5 μm; NMR (CCl_4) δ 7.68 and 7.26 (2 d, 8, C_6H_4), 4.43 (m, 2, OCH), 2.43 (s, 6, $CH_3C_6H_4$), 1.30 (m, 6, CH_2), 1.17 (d, 6, CH_3CHO). Anal. Calcd for $C_{21}H_{28}O_6S_2$: C, 57.25; H, 6.41; S, 14.55. Found: C, 57.44; H, 6.48; S, 14.50.

Synthesis of *cis*- and *trans*-3,7-Dimethyl-1,2-dicarbethoxy-*cis*-1,2-diazacycloheptanes (8). To 1.44 g (0.0341 mol) of NaH (57% mineral oil dispersion which was washed with dried benzene) suspended in 50 mL of dry diglyme were added with stirring 4.07 g (0.0231 mol) of 1,2-dicarbethoxyhydrazine and 10 g (0.0227 mol) of 2,6-heptaneditosylate (7) in succession. The reaction mixture was stirred for 1 h at room temperature and then at 95 °C for 23 h. The white mixture was cooled to 75 °C by the addition of 50 mL of diglyme; 1.44 g (0.0341 mol) of NaH and 15 mL of diglyme were then added. The reaction was allowed to continue at 115–120 °C for 144 h. Finally, the mixture was allowed to reflux at 155–160 °C for 72 h more.

The solids were removed by suction filtration through Celite, 100 mL of water was added, and the solution was extracted with 600 mL of ether (3 × 200 mL) and 300 mL of $CHCl_3$ (3 × 100 mL). The combined organic layers were dried over $MgSO_4$, filtered, and evaporated. Two distillations of the residue afforded 1.67 g (27%) of the cyclic diester: colorless oil; bp 64–65 °C (10^{-4}–10^{-5} mm); n^{28}_D 1.4616; IR (neat) 5.85 (C=O), 7.2 μm (CCH_3); NMR (CCl_3) δ 4.13 (m, 2, CH_3CH), 4.03 (q, 4, CH_2O), 1.57 (s, 6, CH_2), 1.18 (m, 12, CH_3). Anal. Calcd for $C_{13}H_{24}O_4N_2$: C, 57.33; H, 8.88; N, 10.29. Found: C, 57.35; H, 8.89; N, 10.27.

Synthesis of *cis*- (9) and *trans*-3,7-Dimethyl-1,2-diazacycloheptanes (10). A solution of 168 g (2.99 mol) of NaOH dissolved in 321 mL of absolute MeOH was added to 66.5 g (0.244 mol) of a mixture of *cis*- and *trans*-3,7-dimethyl-1,2-dicarbethoxy-*cis*-1,2-diazacycloheptanes, and the mixture was allowed to reflux for 144 h with magnetic stirring. After the mixture was cooled to room temperature, the solids were removed by filtration and washed with a small amount of ether. Excess MeOH was removed under N_2 at a maximum bath temperature of 30 °C before 500 mL of distilled water was added and the solution was subjected to continuous ether extraction for 5 days, again under a blanket of N_2. At the end of the extraction period, the water layer contained in the collection flask was extracted with 400 mL (2 × 200 mL) of ether and 200 mL of $CHCl_3$. The combined organic layers were dried twice under N_2, using an anhydrous mixture of $MgSO_4$ and K_2CO_3. After filtration the solvents were removed on the rotary evaporator under N_2 at room temperature. Two distillations under N_2 through a short-path distillation apparatus afforded 19.7 g (63%) of a mixture of the light yellow dimethyl hydrazines: bp 59–60 °C (20 mm); GLC (20% Carbowax, 150 °C) *trans*-dimethyl isomer (10), 5.52 min (60%), *cis*-dimethyl isomer (9), 6.24 min (40%); $n^{25.5}_D$ 1.4642; IR (neat) 3.05 (NH), 7.25 μm (CCH_3); NMR ($CDCl_3$) δ 2.92 (m, 4, NH buried in CH_3CH), 1.60 (m, 6, CH_2), 1.03 and 0.97 (2 d, 6, J = 7 Hz, CH_3CH). Anal. Calcd for $C_7H_{16}N_2$: C, 65.57; H, 12.58; N, 21.85. Found: C, 65.41; H, 12.43; N, 21.74.

Synthesis of *cis*- (2) and *trans*-3,7-Dimethyl-1,2-diaza-(*Z*)-1-cycloheptenes (3). To 1.00 g (0.00780 mol) of a mixture of *cis*- and *trans*-3,7-dimethyl-*cis*-1,2-diazacycloheptanes in 43 mL of dry THF were added 13.6 g (0.0628 mol) of HgO and a small amount of anhydrous $MgSO_4$. The mixture was stirred at room temperature for 36 h. The solids were removed by filtration through Celite and the solvent was removed under N_2 at room temperature. After lyophilization to remove the last traces of solvent, 0.890 g (90%) of an isomeric mixture of 2 and 3 was obtained: pale yellow oil; $n^{22.5}_D$ 1.4691; IR (neat) 6.4 (N=N), 7.25 μm (CCH_3); NMR ($CDCl_3$) δ 4.47 (m, 1, CH_3CH), 3.75 (m, 1, CH_3CH), 1.70 and 1.48 (2 d, 6, J = 7 Hz, CH_3CH), 1.53 (m, 6, CH_2). Anal. Calcd for $C_7H_{14}N_2$: C, 66.62; H, 11.18; N, 22.20. Found: C, 66.38; H, 11.14; N, 22.02.

Separation of *cis*- (9) and *trans*-3,7-Dimethyl-1,2-diazacycloheptanes (10). After the mixture of hydrazines had been distilled twice through a short-path distillation head, separation was achieved by distillation through a Nester–Faust annular Teflon spinning-band column equipped with an automatic control console. The distillations were carried out by using a nitrogen bleed and a manostat to keep the pressure constant at 20 mm. The manostat was used in conjunction with a high-vacuum pump. Two and sometimes three passes through the column were necessary in order to obtain the pure isomers.

The final distillation was accomplished with a mixture enriched in the desired isomer (>60%) at a reflux ratio of 200:1 with a reflux rate of 6 to 10 drops per minute. A temperature gradient of 10 degrees over the length of the column was most desirable. After equilibrium was obtained by refluxing for 0.25–2 h, distillate was collected for 3 or 4 min before the system was once again allowed to equilibrate. On the average, a spinning-band distillation required 30–35 h.

Compound 10 is a pale yellow liquid: bp 60–61 °C (20 mm); $n^{25.4}_D$ 1.4607; IR (neat) 3.07 (NH), 7.25 μm (CCH_3); NMR ($CDCl_3$) δ 3.05 (s, 2, NH), 2.69 (m, 2, CH_3CH), 1.59 (m, 6, CH_2), 1.07 (d, 6, J = 7 Hz, CH_3). Anal. Calcd for $C_7H_{16}N_2$: C, 65.57; H, 12.58; N, 21.85. Found: C, 65.34; H, 12.50; N, 21.33.

Compound 9 is also a pale yellow liquid: bp 63–64 °C (20 mm); $n^{25.4}_D$ 1.4669; IR (neat) 3.07 (NH), 7.25 μm (CCH_3); NMR ($CDCl_3$) δ 2.87 (s, 2, NH), 2.96 (m, 2, CH_3CH), 1.75 (m, 6, CH_2), 1.00 (d, 6, J = 7 Hz, CH_3). Anal. Calcd for $C_7H_{16}N_2$: C, 65.57; H, 12.58; N, 21.85. Found: C, 65.79; H, 12.62; N, 21.34.

Synthesis of *trans*-3,7-Dimethyl-1,2-diaza-(*Z*)-1-cycloheptene (3). The procedure used was similar to that described for the preparation of the mixture of isomers (2 and 3) using HgO except that the reaction time was only 34 h. A pot-to-pot transfer under high vacuum afforded a 90% yield of pure *trans*-3,7-dimethyl-1,2-diaza-(*Z*)-1-cycloheptene (3): pale yellow liquid; $n^{25.4}_D$ 1.4589; IR (neat) 6.45 (N=N), 7.25 μm (CCH_3); UV (isooctane) λ_{max} 396 nm (ε 152); NMR ($CDCl_3$) δ 3.75 (m, 2, CH_3CH), 1.56

(m, 6, CH_2), 1.73 (d, 6, J = 7 Hz, CH_3). Anal. Calcd for $C_7H_{14}N_2$: C, 66.62; H, 11.18; N, 22.20. Found: C, 66.54; H, 11.16; N, 22.27.

Synthesis of *cis*-3,7-Dimethyl-1,2-diaza-(*Z*)-1-cycloheptene (2). The procedure used was similar to that described above except that the reaction time was only 18 h. Isolation of the product, lyophilization, and a pot-to-pot distillation produced analytically pure *cis*-3,7-dimethyl-1,2-diaza-(*Z*)-1-cycloheptene (2) in 95.5% yield. Compound 2 is a pale yellow liquid: $n^{25.4}_D$ 1.4669; IR (neat) 6.38 (N=N), 7.25 μm (CCH_3); UV (isooctane) λ_{max} 401 nm (ε 85.5); NMR ($CDCl_3$) δ 4.47 (m, 2, CH_3CH), 1.58 (m, 6, CH_2), 1.50 (d, 6, J = 7 Hz, CH_3). Anal. Calcd for $C_7H_{14}N_2$: C, 66.62; H, 11.18; N, 22.20. Found: C, 66.67; H, 11.30; N, 22.14.

Dipole Moment Measurements. A DMO1 dipole meter[13] operating at a fixed frequency of approximately 2.0 MHz and a cylindrical, gold-plated, thermostated cell were used for all dielectric determinations. On the average, five solutions of the compound of varying concentrations in dry cyclohexane (molecular sieves) were used.

Indices of refraction were measured by using a Zeiss dipping refractometer. The same solutions were used for both the dielectric and refractometric measurements. The dipole moments were calculated by using the method of Guggenheim.[14,15]

Europium Shift Experiments. Approximately 25% solutions of the europium shift reagent [Eu(fod)$_3$] in either CCl_4 or $CDCl_3$ were prepared and stored in 5-mL standard septum bottles equipped with Teflon Mininert valves (Thompson Packard, Little Falls, NJ). When not in use, the shift reagent solution was stored in the refrigerator in a jar containing Drierite as desiccant.

In a typical experiment, after 25–50 mg of the substrate was weighed into an NMR tube, 0.3 mL of the solvent was added by syringe, and the NMR spectrum was obtained. Successive 50- to 100-μL portions of the shift reagent were added; the NMR spectrum was recorded after each addition of shift reagent. An average of five points was obtained for each experiment. The ΔEu values were obtained by calculating the slope of the line from a plot of the observed downfield chemical shifts (δ) against the Eu(fod)$_3$/substrate molar ratios.

The chemical shifts of the methyl protons of the shift reagent were obtained in a similar manner. However, the chemical-shift values reported for these methyl protons in the presence of various azo compounds represent the values where the molar ratio Eu(fod)$_3$/substrate is equal to 0.10.

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Registry No. 1, 15391-75-0; 2, 75767-79-2; 3, 75767-80-5; 4, 56485-35-9; 5, 75767-81-6; 6, 5700-00-5; 6·monooxalic acid salt, 75767-82-7; 6·monotartaric acid salt, 75780-67-5; 7, 75767-83-8; 8 (cis), 75767-84-9; 8 (trans), 75767-85-0; 9, 75767-86-1; 10, 75767-87-2; 1,2-dicarbethoxyhydrazine, 4114-28-7; 1,5-dibromopentane, 111-24-0; 2,6-heptanediol, 5969-12-0; 2,6-heptanedione, 13505-34-5.

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One-Step Synthesis of Substituted Tetrathiofulvalenes under High Pressure

Joseph E. Rice and Yoshiyuki Okamoto*

Department of Chemistry, Polytechnic Institute of New York, Brooklyn, New York 11201

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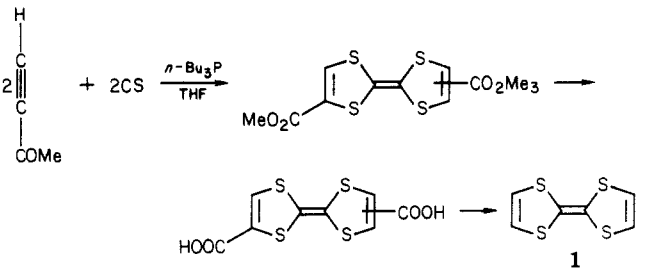
Since the discovery that tetrathiofulvalene (TTF) (1) can form a complex with tetracyanoquinodimethane (TCNQ), which has one of the highest known conductivities of any organic material,[1,2] there has been an enormous amount of research on the synthesis and properties of TTF and its derivatives.[3-6] One of the simplest routes reported for the synthesis of TTF involved the reaction of methyl propiolate with CS_2 in the presence of tributylphosphine.[4]



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THF was employed as the solvent and the reaction was carried out at −30 °C. The yield of the first step was only 21%.

It is a well-known fact that liquid-phase reactions characterized by multiple bond formation are greatly facilitated by the application of hydrostatic pressure.[7] Our interest in this field stems from an ongoing investigation on the application of high pressure to organic synthesis. Thus, we initiated an investigation of the reactions of carboxyl and alkoxylcarbonyl-substituted acetylenes with CS_2 under high pressure in the absence of catalyst.

Results are summarized in Table I. In general, these reactions under high pressure gave rather pure products in good yield. During the reaction of propiolic acid with CS_2, CO_2 was evolved. This was found to be more pronounced at higher reaction temperatures. CO_2 may be formed by the decomposition of the product to TTF.[8] Thus, the yield of the TTF dicarboxylic acid was found to be lower than that of the ester derivatives.

Table I. Reactions of Carboxyl- and Methoxycarbonyl-Substituted Acetylenes with CS_2 under Pressure

reactant	temp, °C	time, h	pressure, atm	% yield
$MeO_2CC{\equiv}CCO_2Me$	100	24	5000	87
$MeO_2CC{\equiv}CCO_2Me$	20	70	4500	0
$MeO_2CC{\equiv}CH$	100	26	5500	96
$MeO_2CC{\equiv}CH$	80	24	4000	88
$MeO_2CC{\equiv}CH$	100	24	100	12
$MeO_2CC{\equiv}CH$	100	24	10	3
$HO_2CC{\equiv}CH$	85	19	5500	69
$HO_2CC{\equiv}CH$	95	25	5500	20
$HO_2CC{\equiv}CH$	100	23	100	12
$HO_2CC{\equiv}CH$	100	22	10	5

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer Model 457

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(8) TTF was obtained by decarboxylation of the dicarboxylic acid derivative in a sealed tube.[4]

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