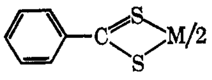

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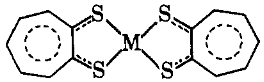
have recently been characterized in detail.[12] Taking Ni(SST)$_2$ and Ni(dtb)$_2$ as examples, their infrared spectra (mull, 1500–400 cm^{-1}) and electronic and mass spectra are markedly different. In particular, Ni(dtb)$_2$ shows only a weak parent ion peak and a fragmentation pattern clearly dissimilar to that of Ni(SST)$_2$. No d–d absorption band such as that at 13,200 cm^{-1} ($\epsilon \sim 980$) observed in the spectrum of Ni(dtb)$_2$[12c] can be found in the spectrum of Ni(SST)$_2$, which in the 11,000–15,000-cm^{-1} range consists of two intense features at 13,500 cm^{-1} (ϵ 14,600) and 15,200 cm^{-1} (sh, $\epsilon \sim 7300$). Further prominent spectral differences between the Ni, Pd, and Pt complexes of the SST and dtb series[12c] are observed in the 15,000–35,000-cm^{-1} region.

The electronic ground-state description of the bisdithiotropolonates represents an interesting problem. Adopting a qualitative valence-bond approach,[8a,13] structures such as **2** in which the metal has the *formal* oxidation state II lead to the delocalized formulation **6**



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for M(SST)$_2$. A probable consequence of the delocalized electronic structure is the observed polarographic reducibility of these complexes. For example, Ni(SST)$_2$ and Pd(SST)$_2$ show one-electron reductions with $E_{1/2}$ -0.69 and -0.67 V,[14] respectively. A second, less well-defined wave is observed at -1.06 (Ni) and -0.98 V (Pd). Zn(SST)$_2$ and Cd(SST)$_2$ exhibit two apparently single-electron reductions at -0.66, -0.88 (Zn) and -0.69, -0.89 V (Cd). This behavior is similar to that now well recognized for other series of complexes containing delocalized five-membered chelate rings, *viz.*, the Ni, Pd, and Pt neutral dithiolenes, $[MS_4C_4R_4]^0$, and 1,2-disubstituted benzenes and derivatives, $[M(C_6H_4XY)_2]^0$ (X, Y = NH, O, S),[8b,13,15] and the Ni, Zn, and Cd complexes $[M(gma)]^0$ and $[M(dtbh)]^0$.[8a] However, the electronic structural features responsible for this behavior may not be the same as those of, *e.g.*, the bisdithiolenes. A *strictly analogous* set of contributing VB structures, which furnish a satisfactory, simple ground-state description of $[MS_4C_4R_4]^0$ species,[13] cannot be written for M(SST)$_2$ complexes.[16] The close similarity of the first reduction potentials of the latter species suggests that in each case the electron is added to a nearly exclusively ligand-based MO whereas the odd-electron MO in species such as $[NiS_4C_4R_4]^-$ has appreciable metal orbital admixture.[8a]

Results presently at hand demonstrate that dithiotropolone is sufficiently stable to be isolated in substance and that it forms stable bis-chelate complexes whose spectral and electrochemical properties, at least of the Ni, Pd, Pt species, imply a delocalized ground-state description of neutral complexes and monoanions. Finally, it is noted that **3** is a potentially useful intermediate for the synthesis of 1,7-disubstituted cycloheptatrienes by nucleophilic reactions. As a further example, reaction of a 1:2:1 mole ratio of **3**, *p*-toluidine, and sodium ethoxide (EtOH, 80°, 48 hr) yields the known N,N′-*p*-tolylaminotroponeimine[2b] in 46% yield. Further details concerning the synthetic utility of **3** and the structural-electronic properties of dithiotropolone and its metal complexes, together with a comparison of these properties with those of the bisdithiolenes, will be reported subsequently.

Acknowledgment. This research was supported by NSF Grant GP-7576X. We thank Drs. J. P. Fackler and E. L. Muetterties for helpful discussion.

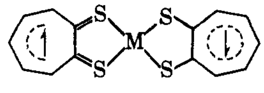
(12) (a) J. P. Fackler, Jr., D. Coucouvanis, J. A. Fetchin, and W. C. Seidel, *J. Am. Chem. Soc.*, **90**, 2734 (1968); (b) M. Bonamico and G. Dessy, *Chem. Commun.*, 483 (1968); (c) C. Furlani and M. L. Luciani, *Inorg. Chem.*, 7, 1586 (1968).

(13) G. N. Schrauzer and V. P. Mayweg, *J. Am. Chem. Soc.*, **87**, 3585 (1965).

(14) Polarographic data were obtained in DMF solution containing 0.1 *M* (Bu$_4$N)(BF$_4$) supporting electrolyte and a rotating platinum electrode; potentials were measured *vs.* sce.

(15) G. N. Schrauzer, *Transition Metal Chem.*, **4**, 299 (1968).

(16) In this connection it is to be noted that, in addition to the ligand-delocalized formulation **6**, other structures, represented collectively by 7, could also be invoked as possible contributors to the electronic



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description of M(SST)$_2$ complexes, particularly of those having a planar stereochemistry. The inclusion of such structures would suggest a ground-state VB description related to that of the neutral, diamagnetic bisdithiolenes,[13,15] but with the difference that odd-electron ligand structures need not necessarily arise in the latter cases. The importance of the structures summarized by 7 and the attendant electronic structural similarities between dithiolenes and dithiotropolonates is currently being investigated. The argument[15] that M(SST)$_2$ species will not possess as high electron affinities as the corresponding dithiolene complexes because of the absence of strictly analogous resonance forms receives support from the potentials reported here.

(17) National Institutes of Health Predoctoral Fellow, 1968–.

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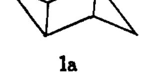
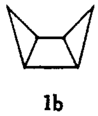
Tricyclo[3.1.0.0^{2,4}]hexane

Sir:

The tricyclo[3.1.0.0^{2,4}]hexane system has received only very limited investigation.[1–4] Moreover, the geometrical isomers of the parent hydrocarbon, **1a** and **1b**, have not been described. We wish to report the synthesis and fundamental characterization of the *trans* isomer **1a**.



1a



1b

Scheme I outlines the synthetic sequence.[5] Treatment of **2**[6] with excess ethereal diazomethane at 0–5° for 3 days provided **3**: 87%; mp 120–121° (from dichloromethane–pentane); $\lambda_{max}^{CH_3OH}$ 323 mμ (ϵ 451) (–N=N–);[7] λ_{max}^{Nujol} 6.45 μ (–N=N–).[7] Compound **3**

(1) C. Deboer and R. Breslow, *Tetrahedron Letters*, 1033 (1967).

(2) N. Obata and I. Moritani, *Bull. Chem. Soc. Japan*, **39**, 2250 (1966).

(3) H. H. Stechl, *Chem. Ber.*, **97**, 2681 (1964).

(4) For a review of such highly strained compounds, see D. Seebach, *Angew. Chem. Intern. Ed. Engl.*, **4**, 121 (1965).

(5) Satisfactory elemental analyses were obtained for **1a**, **3**, and **6–8**.

(6) A. Rodgmann and G. F. Wright, *J. Org. Chem.*, **18**, 465 (1953).

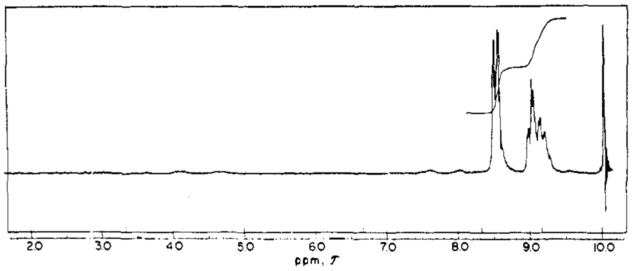
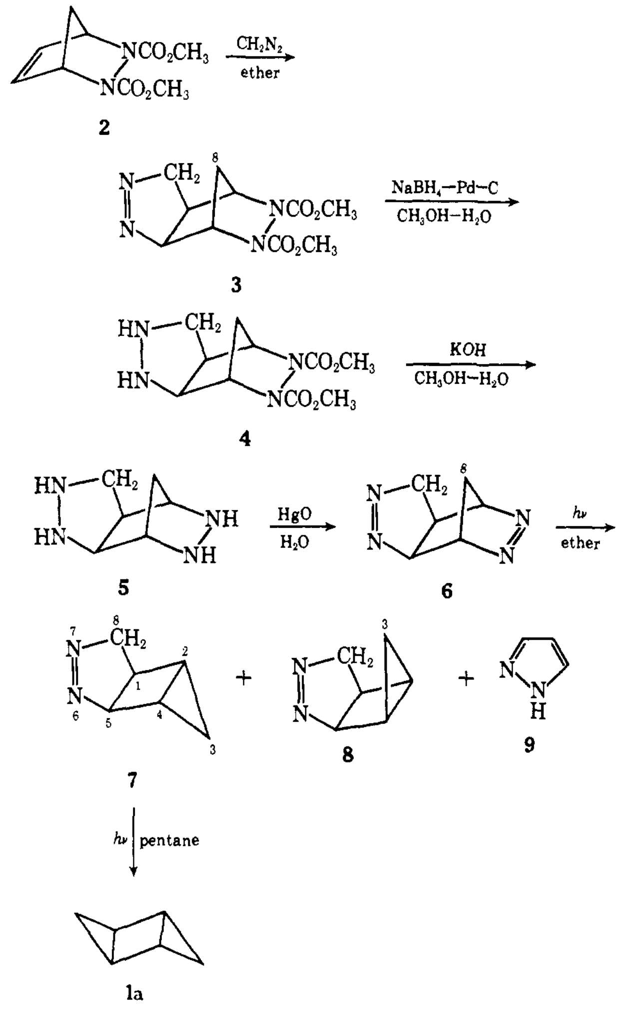


Figure 1. The 60-Mcps nmr spectrum of **1a**; solvent $CDCl_3$, internal standard tetramethylsilane.

is assigned the *exo* configuration on the basis that **2** adds other reagents from the *exo* side of the double bond.[8] This is supported by the fact that the nmr

Scheme I



spectrum of **3** has one C_8 proton signal at τ 9.13. The absorption is upfield >0.7 ppm from the C_7 protons of comparable 2,3-diazabicyclo[2.2.1]heptyl structures.[8,9]

Reduction of **3** with sodium borohydride and palladium–charcoal in aqueous methanol gave the monohydrazine **4**. Hydrolysis–decarboxylation of **4** with hot potassium hydroxide in aqueous methanol[10] led to bishydrazine **5**. Mercuric oxide oxidation in water[10] readily transformed **5** to the bisazo compound **6**: 52% (over-all yield from **3**); mp 105–106° (from 60–90° ligroin); $\lambda_{max}^{CH_3OH}$ 324 (ε 421) and 339 mμ (ε 277) (two different –N=N–);[7,10] λ_{max}^{Nujol} 6.48 and 6.69 μ (two different –N=N–);[7,10] nmr, τ_{CDCl_3} 9.27 (1 H, doublet, J = 12 cps), 8.72 (1 H, doublet with additional splittings, J = 12 cps), 8.03 (1 H, multiplet), 5.72 (2 H, multiplet), 5.19 (1 H, multiplet), 4.95 (1 H, multiplet), and 4.22 (1 H, multiplet).

A degassed solution of **6** in ether was irradiated with 3500-Å light[11] until 1 equiv of nitrogen had been evolved. Glpc analysis showed a mixture of three components in the ratio of 85:11:4. These were identified as **7**, **8**, and **9**, respectively. The three compounds were readily separated by preparative glpc (Carbowax 20M on Chromosorb W column). The *trans*-monoazo isomer **7** is characterized by bp 86–87° (28 mm); λ_{max}^{hexane} 324 mμ (ε 458);[7] λ_{max}^{neat} 6.47 μ (–N=N–);[7] nmr, τ_{CDCl_3} 9.25 (2 H, multiplet), 8.74 (1 H, multiplet), 8.12 (2 H, multiplet), 5.69 (2 H, multiplet), and 5.25 (1 H, multiplet). The *cis*-monoazo isomer **8** shows λ_{max}^{hexane} 337 (ε 252) and 331 mμ (sh) (ε 244); λ_{max}^{neat} 6.52 μ (–N=N–); nmr, τ_{CDCl_3} 10.23 (1 H, doublet of triplets), 9.74 (1 H, quartet with additional small splitting), 8.64 (1 H, quartet with additional small splittings), 8.26 (1 H, quartet with additional small splittings), 7.74 (1 H, multiplet), 6.30 (2 H, four-line pattern), and 4.92 (1 H, multiplet). Assignment of *cis* and *trans* configurations to **8** and **7**, respectively, follows from **8** having a C_3 proton at *ca.* 1.0-ppm higher field than **7**.[7,9] Compound **9** has physical and spectral properties identical with authentic pyrazole.

A degassed 0.01 *M* solution of **7** in pentane was irradiated with 3100-Å light until nitrogen evolution ceased. This produced tricyclohexane **1a** as the major volatile product (*ca.* 10–15% yield) along with much smaller amounts of 1,4-cyclohexadiene and two other unidentified compounds. Isolation of pure **1a** was achieved by preparative glpc at room temperature with a 5 ft × 0.25 in. column packed with 20% Hallcomid M-18-OL on Chromosorb W.

Spectral data clearly indicate tricyclo[3.1.0.0^{2,4}]hexane. Olefinic structures are excluded by the nmr spectrum which shows no resonances below τ 8.4 (Figure 1). Absorption above τ 9 is consistent with cyclopropyl methylene protons. The ir spectrum has the expected characteristic cyclopropyl absorptions in the 3.25–3.3- and 9.3–9.9-μ regions;[12] λ_{max}^{neat} 3.27 (vs),[13] 9.47 (s), and 9.90 (s) μ. Mass spectral analysis shows the parent peak at m/e 80.

In order to confirm the gross skeletal structure chemically, **1a** was hydrogenated over platinum oxide in acetic acid. Reduction proceeded smoothly at room temperature and atmospheric pressure to produce cyclohexane and methylcyclopentane in a 70:30 ratio. The two products were identified by glpc

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(7) R. J. Crawford, A. Mishra, and R. Dummel, *J. Am. Chem. Soc.*, **88**, 3959 (1966).

(8) E. L. Allred, C. L. Anderson, and R. L. Smith, *J. Org. Chem.*, **31**, 3493 (1966).

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(10) S. G. Cohen, R. Zand, and C. Steel, *J. Am. Chem. Soc.*, **83**, 2895 (1961); S. G. Cohen and R. Zand, *ibid.*, **84**, 586 (1962).

(11) RPR 3500-Å lamps in a Rayonet photochemical reactor.

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(13) This is the strongest absorption in the ir spectrum.

retention times and nmr spectral comparison with authentic specimens.

The assignment of the *trans* configuration **1a** to this tricyclohexane follows from the method of synthesis and the fact that the precursor **7** has the C_8 carbon locked *trans* to the fused cyclopropyl ring.

In preliminary experiments we have observed that **1a** is recovered unchanged after 2 hr at 100°; however, it is converted to *ca.* 50% 1,4-cyclohexadiene in 3 hr at 165°. Highly strained bicyclo[2.1.0]pentane and bicyclo[1.1.0]butane[14] have thermal rearrangement 3-hr half-lives at *ca.* 270[15] and 214°,[16] respectively. This stability comparison indicates that the intrinsic strain of **1a** is very high.

Further investigation of the physical and chemical properties of **1a** is in progress. We also are investigating the possibility of converting **8** to the *cis* isomer **1b**.

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[14] R. B. Turner, P. Goebel, B. J. Mallon, W. von E. Doering, J. F. Coburn, and M. Pomerantz, *J. Am. Chem. Soc.*, **90**, 4315 (1968).

[15] Estimated from the data of M. L. Halberstadt and J. P. Chesick, *ibid.*, **84**, 2688 (1962).

[16] Estimated from the data of H. M. Frey and I. R. D. Stevens, *Trans. Faraday Soc.*, **61**, 90 (1965).

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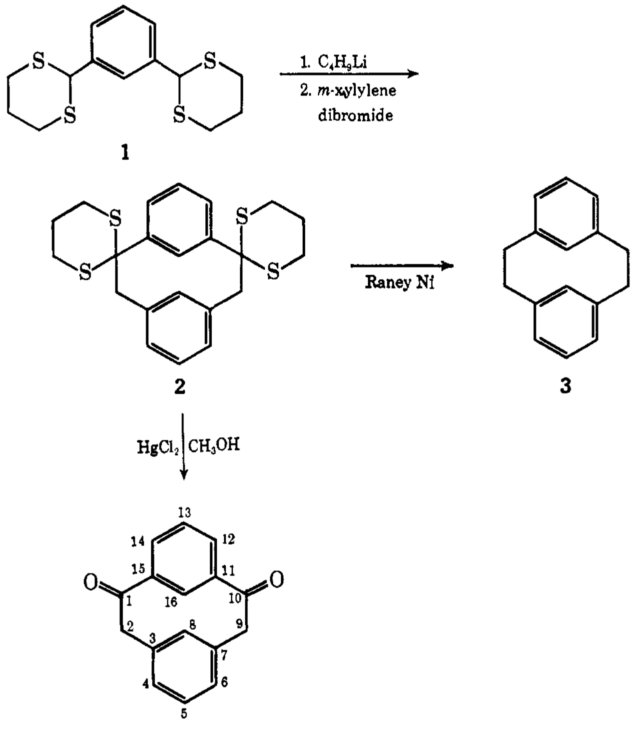
A New Method of Synthesis of Cyclophanes. [2.2]Metaparacyclophane-1,9-diene

Sir:

Of the methods investigated for preparing cyclophanes, the Wurtz reaction has proved to be the most general and useful procedure, especially for cyclophanes having a two-carbon bridge.[1,2] The yields in a Wurtz dimerization are modest, usually being about 30%, and the choice of compounds is very limited due to the severity of the reaction conditions.[3,4] Also, the Wurtz reaction has generally been limited to the synthesis of symmetrical cyclophanes.[5] In our studies on the synthesis of unusual aromatic molecules,[6-8] we have been concerned with the syntheses of [2.2]-metacyclophanes as intermediates and how to introduce unsaturation into the two-carbon bridges.[9] We now report a method that appears to be general for the synthesis of cyclophanes and which retains functionality in the bridges that can later be converted to olefinic unsaturation.

Corey and Seebach introduced the use of 1,3-dithianes for the synthesis of ketones,[10] and recently they have described the stepwise synthesis of diketones.[11] We have investigated the reaction of the dianion derived from isophthalaldehyde bis(1,3-propanedithioacetal) (**1**) with *m*-xylylene dibromide and have found that the corresponding [2.2]metacyclophane derivative (**2**) is formed in 28% yield. As proof of structure, **2** was treated with Raney nickel and converted in 68% yield to [2.2]metacyclophane (**3**), identical in all respects with an authentic sample.



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The preparation of **1** was readily accomplished in quantitative yield by heating isophthalaldehyde with 1,3-propanedithiol in benzene containing a small quantity of *p*-toluenesulfonic acid. After recrystallization from a benzene–hexane mixture, **1** separated as white needles, mp 129.0–129.5°.[12] Formation of the metacyclophane **2** was carried out by treating **1** in tetrahydrofuran at −30° under a nitrogen atmosphere with 2 mol of *n*-butyllithium followed by dropwise addition of a solution of *m*-xylylene dibromide in tetrahydrofuran. After isolation and chromatography over silica gel, **2** was recrystallized from a benzene–hexane mixture to give white rhombic crystals, mp 242.0–243.5°. In addition to its conversion to [2.2]metacyclophane, **2** was hydrolyzed by heating with mercuric chloride in a methanol–tetrahydrofuran mixture in a sealed tube at 130° for 7 hr, followed by boiling the resulting dimethyl ketal in a solution of acidic aqueous acetone. This gave the diketone **4** in 42% yield as white needles, mp 144.0–144.5°. With regard to the spectral properties of **4**, the carbonyl frequency in the infrared is normal, appearing at 5.90 μ; the signals for the protons at the

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[3] S. Akabori, T. Sato, and K. Hata, *J. Org. Chem.*, **33**, 3277 (1968).

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[5] For an exception, though, see V. Boekelheide, C. Ramey, E. Sturm, T. Miyasaka, and B. A. Hess, Jr., *ibid.*, in press.

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[7] V. Boekelheide and J. B. Phillips, *ibid.*, **89**, 1695 (1967).

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[10] E. J. Corey and D. Seebach, *Angew. Chem.*, **77**, 1134, 1135 (1965).

[11] D. Seebach, N. R. Jones, and E. J. Corey, *J. Org. Chem.*, **33**, 300 (1968).

[12] Satisfactory elemental analyses have been obtained for all new compounds.