of the methyl group,[18] which allows it to be forced into the cavity of the folded form, **1** ($X = CH_3$, $Y = H$) (F) with consequent partitioning of the bond relocation along both possible paths, A and B, with a slight preference (70:30) for A.[19]

Acknowledgment. We wish to thank the National Science Foundation (GP-26347) and the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

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(18) For a rational explanation as to why a syn methyl substituent o a monomethyl bridge ought to be sterically "smaller" than one associated with a dimethyl group see ref 4.

(19) Perhaps it is worth stressing here that the present invalidation of the criticism leveled at this interpretation serves as a clear warning against the use of readily available, but improperly substituted compounds as models for securing mechanistic information about skeletal transformations of hydrocarbons. This cautionary note is perhaps best exemplified by the exclusive thermal bond relocation of 9-methyl-9-cyanobicyclo[6.1.0]nona-2,4,6-triene[20] and its dicyano analog[21] into a [4.2.1] rather than [4.3.0] skeleton.

(20) F. G. Klärner, *Tetrahedron Lett.*, 3611 (1971).

(21) A. G. Anastassiou, R. P. Cellura, and E. Ciganek, *Tetrahedron Lett.*, 5267 (1970).

(22) National Science Foundation Graduate Trainee, 1969–present.

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Thermal Rearrangement of *cis*-Bicyclo[6.1.0]nona-2,6-dienes

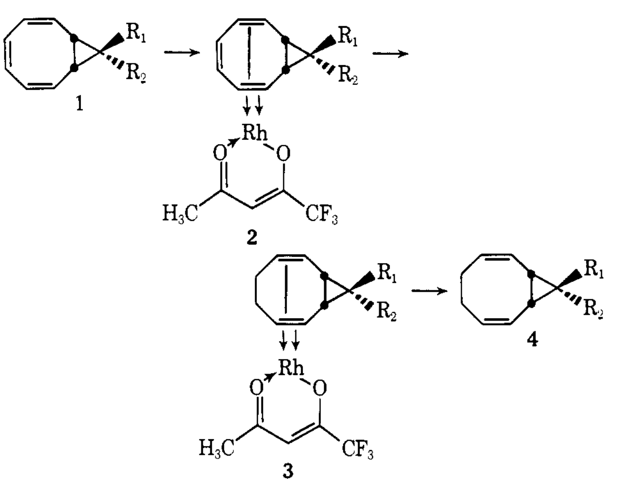
Sir:

Recently the protection of suitably located double bonds in catalytic hydrogenations by means of the trifluoroacetylacetonatorhodium group has been demonstrated.[1] This synthetic method, when applied to *cis*-bicyclo[6.1.0]nona-2,4,6-trienes, makes the corresponding *cis*-bicyclo[6.1.0]nona-2,6-dienes readily accessible.

According to Scheme I the trienes **1a–d**[2] were transformed into the trifluoroacetylacetonatorhodium(I) complexes **2a–d** by treatment with dicarbonyltrifluoroacetylacetonatorhodium in hexane solution. The free double bond in these complexes was hydrogenated in hexane solution with 5% Pd/C, and the olefinic ligand was set free from the resulting complexes **3a–d** by shaking a pentane solution with 10% aqueous KCN. Data for the individual reaction steps are listed in Table I.

The *cis*-bicyclo[6.1.0]nona-2,6-dienes **4a–d** thus obtained undergo thermal rearrangement to the respective *cis*-bicyclo[5.2.0]nona-2,5-dienes **5a–d** under distinctly different conditions.

Scheme I

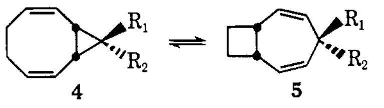


a, $R_1 = H$; $R_2 = H$
b, $R_1 = CH_3$; $R_2 = H$
c, $R_1 = H$; $R_2 = CH_3$
d, $R_1 = CH_3$; $R_2 = CH_3$

Table I. Selective Reduction of *cis*-Bicyclo[6.1.0]nonatrienes

Starting triene	Yield (%) (mp, °C) of intermediates 2	3	Yield (%) and ^1H nmr data[a] of product 4	R_1	R_2
1a	94.5 (64)	88 (67)	85[b]	9.18, t of d (9; 3.5)	9.98, t of d (6.5; 3.5)
1b	88.5 (89)	90.5 (105)	76[b]	8.85, d (6)	9.63, q (6)
1c	93 (87)	88 (98)	68	8.8–9.2, m	9.10, d (2.5)
1d	97 (109)	86.5 (110)	82	8.86, s	9.10, s

[a] Reported are the shifts (τ) and coupling constants (Hz) of the groups R_1 and R_2, determined in CCl_4 solution with benzene as internal standard at 100 MHz; other signals are in accord with the structure. [b] Liberation and work-up at 0°.



4 5

Whereas **4a**[3] and its *anti*-9-methyl derivative **4b** undergo the Cope rearrangement to **5a**[4] and **5b**, respectively, already at room temperature, the *syn*-9-methyl compound **4c** requires 150° for its transformation into **5c** and the *gem*-dimethyl compound **4d** rearranges only above 180°. In the latter case a by-product, believed to be 3-(2-propenyl)cycloocta-1,4-diene, appears for whose formation a competing homopentadienyl hydrogen shift[4,5] in **4d** can be envisioned. The unidirectional Cope rearrangement of the parent compound **4a** turns reversible in the methyl derivatives **4b–d**. This stabilization of a cyclopropane ring by methyl substitution is well documented both by theory[6] and experiment.[7] Judging from the equilibrium constants for the isomerization of 1-methylbarbaralone[7] and of dienes **4b–d** (see Table II), a methyl group favors a cyclopropane ring over a bisallylic position by 0.7–2.5 kcal/mol in free energy. Accordingly, the parent compound **4a** already must be close to equilibrium with **5a**.

The stereospecificity of the rearrangement follows from the fact that epimeric products arise from **4b** and

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(1) W. Grimme, *J. Amer. Chem. Soc.*, **94**, 2525 (1972).

(2) (a) E. Vogel and H. Kiefer, *Angew. Chem.*, **73**, 548 (1961); (b) T. J. Katz and P. J. Garratt, *J. Amer. Chem. Soc.*, **86**, 4876 (1964); (c) P. Radlick and W. Fenical, *ibid.*, **91**, 1560 (1969); (d) J. Esser, Diplomarbeit, University of Cologne, 1968; (e) S. W. Staley and T. J. Henry, *J. Amer. Chem. Soc.*, **91**, 1239 (1969).

(3) The synthesis of 4a by a more laborious route and its rearrangement have been reported: M. S. Baird and C. B. Reese, *Chem. Commun.*, 1519 (1970).

(4) W. R. Roth, *Justus Liebigs Ann. Chem.*, **671**, 10 (1964).

(5) (a) W. Grimme, *Chem. Ber.*, **98**, 756 (1965); (b) D. S. Glass, R. S. Boikess, and S. Winstein, *Tetrahedron Lett.*, 999 (1966).

(6) N. Trinajstić and M. Randić, *J. Chem. Soc.*, 5621 (1965).

(7) J. C. Barborak, S. Chari, and P. von R. Schleyer, *J. Amer. Chem. Soc.*, **93**, 5275 (1971).

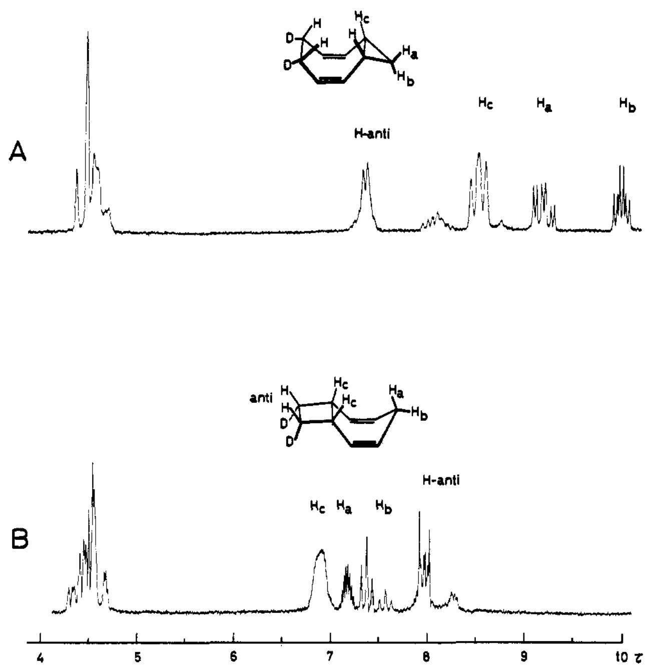


Figure 1. Proton nmr spectrum of deuterium labeled diene **4a**-d_2 (A) and of its Cope rearrangement product **5a**-d_2 (B). Both spectra are taken in 10% CCl_4 solution at 100 MHz with benzene as internal standard and with H,D decoupling. A small signal due to *syn*-methylene protons from H,D exchange in the synthesis of **4a**-d_2 appears in A around τ 8.1 and in B around τ 8.25.

Table II. Cope Rearrangement of *cis*-Bicyclo[6.1.0]nonadienes

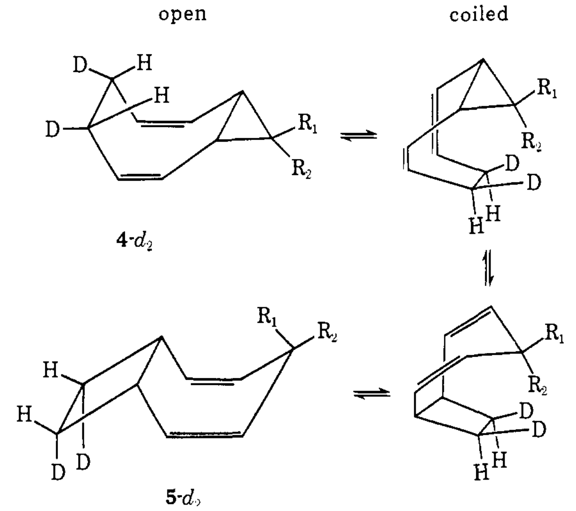
Compd	Temp, °C	10^4k_1, sec^{-1}	*K*	^1H nmr data[a] of product **5** R$_1$	R$_2$
4a	40	0.62[b]		7.05, d of t of t (19)[e]	7.45, d of t (19; 5.5)[e]
4b	40	1.3[b]	6.7	8.87, d (7)	6.5–7[f]
4c	170	0.31[c]	11.5	6.5–7[f]	8.92, d (7.5)
4d	200	0.63[c]	0.7[d]	8.87; 8.83, two s	

[a] Reported are the chemical shifts (τ) and coupling constants (Hz) of groups R$_1$ and R$_2$, determined in CCl_4 solution with benzene as internal standard at 100 MHz; other signals are in accord with the structure. [b] Determined by nmr in *ca.* 10% CCl_4 solution. [c] Determined by glpc analysis of a *ca.* 20% toluene solution. [d] Obtained as quotient of rate constants. [e] Assignment follows from the allylic coupling constants J_3 and J_4; *cf.* E. W. Garbisch, *J. Amer. Chem. Soc.*, **86**, 5564 (1964). [f] Obscured by the signal of the bridgehead protons.

4c. A configurational correlation was obtained with the help of 4,5-dideuterio-*cis*-bicyclo[6.1.0]nona-2,6-diene (**4a**-d_2) (Scheme II) which was synthesized by using deuterium gas instead of hydrogen in the reaction sequence of Scheme I.

In the nmr spectrum of **4a**-d_2 (Figure 1A) only the methylene protons of the eight-membered ring absorbing at low field appear. Accordingly, deuterium has added cis to the free double bond and the remaining methylene protons are in the anti positions, from which they reach—in the open conformation—into the deshielding cones of the flanking double bonds.[8] Confirming the stereospecificity of the reaction, the rearrangement product **5a**-d_2 shows in the nmr spectrum (Figure 1B) only one type of methylene proton at the cyclobutane ring which absorb at low field. Their strong coupling with the neighboring bridgehead protons ($J_{AX} + J_{AX'}$ = 10.4 Hz) indicates the mutual cis orientation,[9] *i.e.*, the cyclobutane methylene protons occupy the anti positions in **5a**-d_2.

Scheme II



The observed transformation of the methylene protons anti to the three-membered ring in **4a**-d_2 into those anti to the cycloheptadiene ring in **5a**-d_2 demands that the transition state is attained from the coiled conformation of *cis*-bicyclo[6.1.0]nona-2,6-diene. This geometry explains the high temperature required for the rearrangement of **4c** and **4d**, as their *syn*-methyl group causes a severe compression. In fact, while for **4c** the stereochemistry of thermolysis implies passage over the coiled transition state, the same is not true for **4d**. Here the higher temperature, leading to a competitive hydrogen shift, might open the alternative diradical pathway. As above, the mechanism was elucidated by deuterium labeling. When *syn*-5,6-dideuterio-9,9-dimethyl-*cis*-bicyclo[6.1.0]nona-2,6-diene (**4d**-d_2), synthesized by the standard sequence of Scheme I, was subjected to a flash pyrolysis (470°, 2 sec) the Cope product **5d**-d_2 and the recovered starting material both showed in the nmr spectrum only the *anti*-methylene protons at the four- or eight-membered ring, respectively. Thus, the transition state derived from the coiled conformation is indeed attained in all of the Cope rearrangements reported here, regardless of the distortion energy involved.

The pronounced retardation of the rearrangement by a *syn*-9-methyl group is well explained as arising from compression in the prerequisite coiled conformation. The further lowering of the rate in the *gem*-dimethyl compound **4d** is in the right order of magnitude as to be related linearly to the decrease in the free energy of isomerization. It is not clear why this decrease in $\Delta\Delta F_f{}^\circ$ exerted by the *anti*-9-methyl group is not reflected in the rate of **4b**, also.

The observed order of reactivity for the *cis*-bicyclo-[6.1.0]nona-2,6-dienes, *i.e.*, *anti*-methyl > unsubstituted > *syn*-methyl > *gem*-dimethyl, is the same as that of the respective trienes **1a–d**.[10] Here, the rearrangement of the monomethyl epimers to the same mixture of the 1-methyl-*cis*-3a,7a-dihydroindenes has been rationalized

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[8] For a review see L. M. Jackman and S. Sternhell, "Application of NMR Spectroscopy in Organic Chemistry," 2nd ed, Pergamon Press, Elmsford, N. Y., 1969, p 83.

[9] *Cf.* the coupling constants in 4,4,5,5-*syn*-9,10-hexadeuterio-*cis*-bicyclo[6.2.0]deca-2,6-diene and citation 10 in ref 1.

[10] A. G. Anastassiou and R. C. Griffith, *Chem. Commun.*, 1301 (1971).

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

Acknowledgments. Financial support provided by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie as well as a generous gift of cyclooctatetraene by the Badische Anilin und Sodafabrik, Ludwigshafen, are gratefully acknowledged.

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

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

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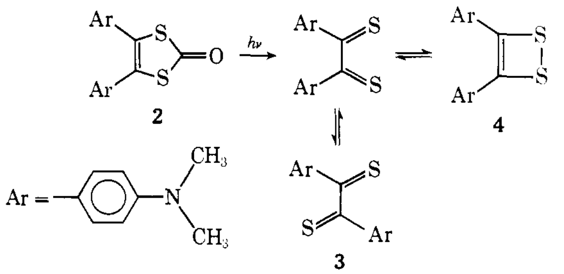
Thione Photochemistry. Preparation of an α-Dithione and the α-Dithione–1,2-Dithiete Equilibrium[1,2]

Sir:

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

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



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

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

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

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

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(1) Photochemical Synthesis. 52. This is No. 11 in a series on thione photochemistry.

(2) Publication No. 67 from the Photochemistry Unit, The University of Western Ontario.

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

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

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

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

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

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

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

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

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

(12) The preparation of this compound will be described elsewhere.

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