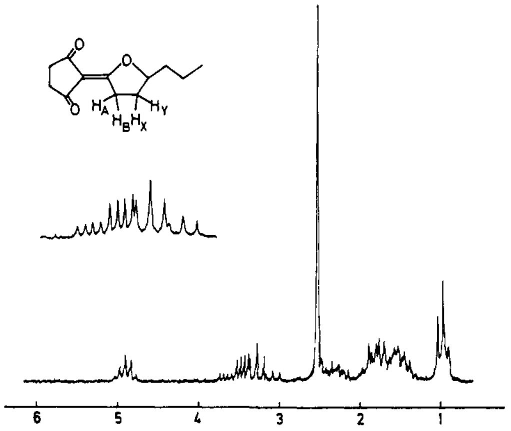
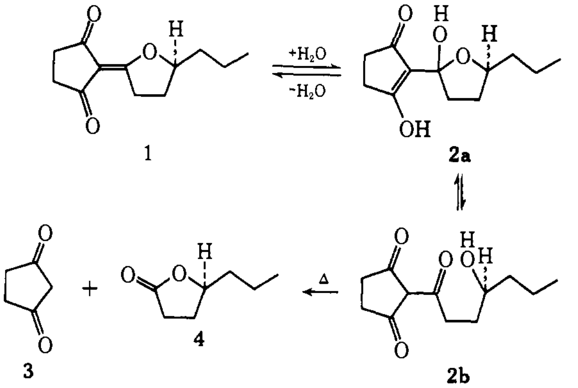


Figure 1. Nmr spectrum of oudenone (1) in $CDCl_3$ at 100 MHz.

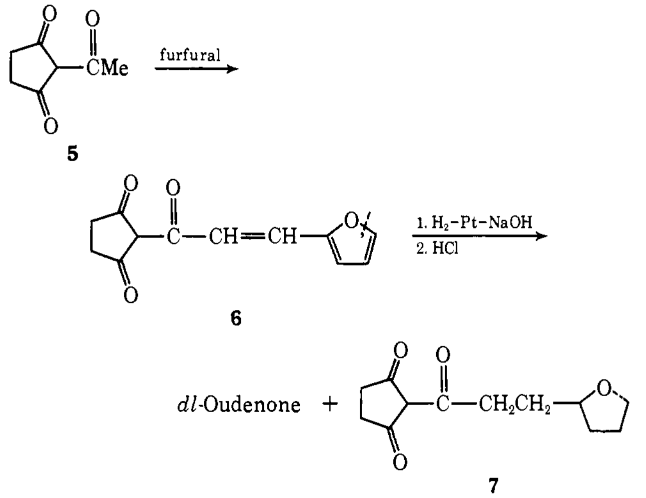
is compatible with the above spectral evidence and has been confirmed by the application of double and triple resonance technique.

Chart I



Ozonolysis or oxidation with $KMnO_4$ afforded succinic acid and γ-propylbutyrolactone[5] (4), showing that the singlet at δ 2.53 corresponds to four hydrogens of succinic acid. Finally, hydrolysis of 1 at 150° in a sealed tube split it into two known fragments without loss of any carbon affording 1,3-cyclopentanedione[6] (3) and the γ-lactone[7] (4).

By combining the above chemical and spectral results and mechanistic considerations, structure 1 has been proposed for oudenone, and the acidic property and positive iodoform test characteristic of oudenone can be reasonably explained by the β-trione structure 2b which is well demonstrated by spectral data (ir, uv, and nmr) and by conversion into the metal salts.[8] The Hudson–Klyne lactone rule[9] permits assignment of the *S* configuration to γ-propylbutyrolactone, since the γ-lactone has negative rotation[7] and negative Cotton effect. Therefore, the absolute structure of oudenone is (*S*)-2-[4,5-dihydro-5-propyl-2(3*H*)-furylidene]-1,3-cyclopentanedione.



The synthetic approach to oudenone was designed to prove the most interesting feature of oudenone or the dynamic skeletal change between structures 1 and 2.

2-Acetyl-1,3-cyclopentanedione[6] (5) was condensed with furfural in the presence of morpholine to afford a condensation product 6 in excellent yield. Hydrogenation over Pt in the presence of 1 mol equiv of sodium hydroxide followed by neutralization with hydrochloric acid afforded *dl*-oudenone[10] in good yield along with 2-[3-(2-tetrahydrofuryl)propionyl]-1,3-cyclopentanedione (7). The racemic oudenone was resolved with brucine hydrate. It should be mentioned here that *dl*-oudenone and *d*-oudenone have equally strong activity inhibiting tyrosine hydroxylase and reducing blood pressure as *l*-oudenone.

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[5] E. Schwenk, D. Papa, H. Hankin, and H. Ginsberg, "Organic Syntheses," Collect. Vol. III, Wiley, New York, N. Y., 1955, p 742.

[6] F. Merényi and M. Nilsson, *Acta Chem. Scand.*, 17, 1801 (1963).

[7] The ir and nmr spectra were confirmed to be identical with those of authentic samples described in ref 5 and 6. The γ-lactone from ozonolysis and hydrolysis has $[\alpha]^{21}D$ −47.2° (*c* 1.08, $CHCl_3$) and −45.0° (*c* 0.78, $CHCl_3$), respectively, providing evidence to support that the mechanism of ring opening of 1 is Michael addition of water followed by the opening of the ether linkage to keep retention of the asymmetric center, as shown in Chart I.

[8] For instance, the treatment of 1 with sodium hydroxide afforded the sodium salt, mp 145–148°, a crystalline powder with satisfactory elemental analysis.

[9] W. Klyne, P. M. Scopes, and A. Williams, *J. Chem. Soc.*, 7237 (1965).

[10] The identity of the racemic form with the natural one was confirmed by spectroscopic data such as ir, uv, and nmr.

Theories of the Isotropic Shift in Complexes with T Ground States. An Experimental Test

Sir:

The use of nuclear magnetic resonance in studying structural, electronic, and chemical problems in paramagnetic transition metal complexes has developed[1] remarkably in recent years. With the widening scope and utility of this technique, the early equations[2] which relate the observed nmr shift to the contact and dipolar interactions have been modified and ex-

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[1] D. R. Eaton and W. D. Phillips, *Advan. Magn. Resonance*, 1, 103 (1965); E. DeBoer and H. van Willigen, *Progr. Nucl. Magn. Resonance Spectrosc.*, 2, 111 (1967); R. H. Holm, *Accounts Chem. Res.*, 2, 307 (1969).

[2] H. M. McConnell and R. E. Robertson, *J. Chem. Phys.*, 29, 1361 (1958).

tended.[3–5] Though each improvement attempted to remove some previous restriction on the applicability of the equations to a particular metal ion, each new theory increased the complexity of the equations and increased the number of required parameters. We wish to present here some data which for the first time allow us to experimentally assess the relative merits and applicability of the various theories as applied to the complexes of divalent cobalt. The specific complexes of interest will be the bis[tris(1-pyrazolyl)borate]-cobalt(II) chelates[6] of the form $(RB(pz)_3)_2Co$. The octahedral $^4T_1$ ground state is split into six well-separated Kramers doublets under the influence of a trigonal distortion and spin–orbit coupling, and several levels of this manifold may be populated in the accessible temperature range. The magnetic properties of each level, as well as the spacings between the levels, are known[7] from independent esr and optical studies. Since all the parameters necessary for the most complex theory are known, these complexes represent the ideal test for the applicability or necessity of the various theories.

The original work of McConnell and Robertson[2] treated the simplest case, namely a single orbitally nondegenerate state with spin S, and obtained the most widely used equations which predict Curie (T^{-1}) behavior for both the contact and dipolar shifts. Unfortunately, for those systems to which these equations are strictly applicable, the magnetic anisotropy is usually not expected to be large enough to produce observable dipolar shifts in the presence of the more important contact interaction. Golding[3] first addressed the problem encountered with T ground states with incompletely quenched orbital angular momentum. He obtained equations for the contact shifts, which considered the excited states and their mixing in the magnetic field. The dipolar term, however, was not treated. Though the inapplicability of the early dipolar equations to Co(II) systems was recognized,[8] most analyses of the dipolar shifts centered around various empirical methods. Jesson[9] derived a set of equations for both the contact and dipolar interactions for trigonal Co(II) complexes, which took into account the thermally accessible states, but neglected second-order Zeeman interactions. Since the various Kramers doublets are known[7] to exhibit different g tensors, the temperature-dependent population of the accessible states produced an overall non-Curie behavior for both contact and dipolar contributions, although the shifts for any one state followed the Curie law.

Kurland and McGarvey[5] developed general equations for treating the dipolar and contact interactions which include the second-order Zeeman interaction. Using this theory, McGarvey[10] has recently calculated the contact and dipolar shifts for trigonal cobalt(II), and applied these equations to the $(RB(pz)_3)_2Co$ complexes. His equations predict that, while the contact shifts approximately follow the Curie law because of the cancellation of non-Curie contributions from the first- and second-order terms, the dipolar shift should deviate sharply from Curie behavior. The calculated dipolar shift agreed[10] well with the observed[9] value at 30°. Recently, sizable deviations from Curie behavior have been observed[11] for some related trigonal Co(II) chelates, where it was possible to correlate the extent of the deviation from T^{-1} behavior with the empirically derived dipolar contribution to the shift.

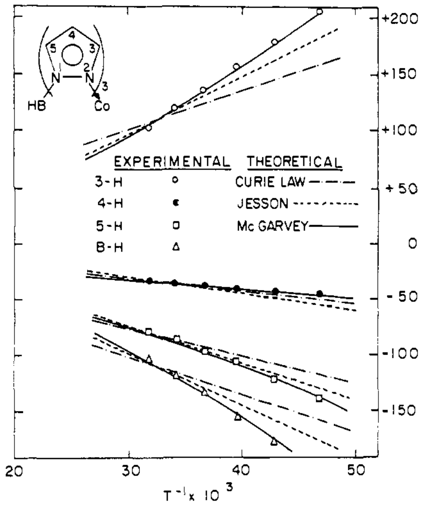

Figure 1. Temperature dependence of isotropic shifts for the complex $[HB(pz)_3]_2Co$ in CD_2Cl_2 compared with curves derived from the Curie law and the equations of Jesson and of McGarvey.

As a critical test of the various theories, we have measured[12] the isotropic shifts for these $(RB(pz)_3)_2Co^{II}$ chelates as a function of temperature. In Figure 1 we compare the experimental[13] data with the temperature dependences predicted by the Curie law, and with the theories of Jesson[4] and McGarvey.[10] Inspection of Figure 1 reveals that the fit between McGarvey's equations and the data points[14] is excellent, while the other two theories are obviously deficient. Generally, the Curie law produces the poorest fit, though the Jesson equations fail to predict the direction of the deviation from Curie behavior for the 4-H shift.

We therefore conclude that in order to quantitatively interpret or calculate dipolar shifts for distorted complexes with T ground states, in particular Co(II), the Kurland–McGarvey equations[5] must be used. The lack of the necessary magnetic and optical data can generally be overcome by utilizing the experimental susceptibility

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(3) R. M. Golding, *Mol. Phys.*, **8**, 561 (1964).

(4) J. P. Jesson, *J. Chem. Phys.*, **47**, 579 (1967).

(5) R. J. Kurland and B. R. McGarvey, *J. Magn. Resonance*, **2**, 286 (1970).

(6) S. Trofimenko, *J. Amer. Chem. Soc.*, **88**, 1842 (1966).

(7) J. P. Jesson, *J. Chem. Phys.*, **45**, 1049 (1966).

(8) W. D. Horrocks, Jr., R. H. Fischer, J. R. Hutchison, and G. N. La Mar, *J. Amer. Chem. Soc.*, **88**, 2436 (1966).

(9) J. P. Jesson, *J. Chem. Phys.*, **47**, 582 (1967).

(10) B. R. McGarvey, *ibid.*, **53**, 86 (1970).

(11) G. N. La Mar and G. R. Van Hecke, *J. Amer. Chem. Soc.*, **92**, 3021 (1970).

(12) Nmr spectra were recorded on a Varian HR-100, using a precalibrated V-4343 temperature-control unit.

(13) The plot for the Curie law was obtained by simply drawing a line through the observed shift at 30° and the origin. For the Jesson and McGarvey theories, the experimentally separated dipolar and contact shifts were taken[14] from ref 9, and the theoretical temperature dependence was generated by eq 7 and 12 of ref 4, and from Figures 1 and 2 of ref 10. Essentially identical lines are obtained for the McGarvey theory using the calculated dipolar shift (ref 10). Similar fits were also obtained for substituted complexes.

(14) A recent X-ray structure of $(HBpz_3)_2Co$, M. R. Churchill, K. Gold, and C. E. Maw, Jr., *Inorg. Chem.*, **9**, 1597 (1970), necessitates recalculation of the geometric factors, $(3\cos^2\chi - 1)/r^3$, leading to values of $-0.02322:-0.00197:0.00838:0.02335$ for 3-H:4-H:5-H:B-H. The geometric factor for p-H in the terminal phenyl group, from which all other dipolar shifts are calculated, is 0.003110. The theoretical lines in Figure 1 are essentially unaffected by changes in geometric factors of ±7%.

tensor.[15] It should be noted that temperature studies of the type described here are necessary to test critically the various theories. The equations of Jesson and of McGarvey can both give reasonable agreement with observed room temperature shifts. It is only when the temperature data are available that the deficiencies of the former set are experimentally demonstrable.

[15] W. D. Horrocks, Jr., *Inorg. Chem.*, **9**, 690 (1970).

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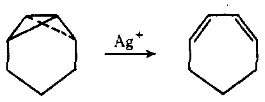
Silver(I) Ion Catalyzed Rearrangements of Strained σ Bonds. V. Stereochemical and Kinetic Analysis of the Isomerization of Bicyclo[1.1.0]butanes[1]

Sir:

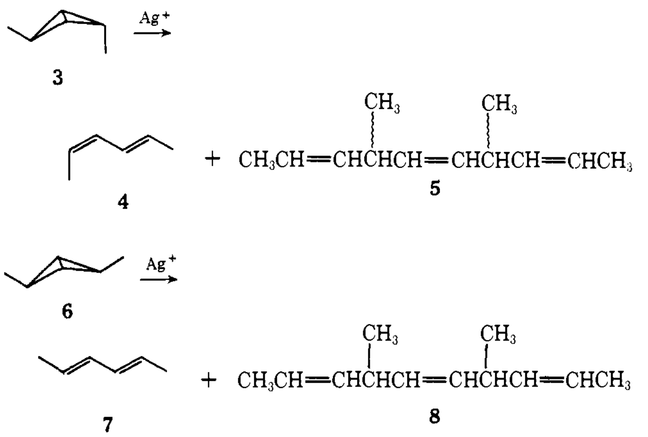
Recent reports from this and other laboratories have described the remarkable capability of silver(I) ion to promote facile $[_\sigma2_a + {}_\sigma2_a]$ skeletal rearrangement of cubyl,[2] homocubyl,[3] 1,1′-bishomocubyl,[3,4] and secocubyl systems.[5] We have also described the ready isomerization of tricyclo[4.1.0.0^{2,7}]heptane (**1**) to *cis*,*cis*-1,3-cycloheptadiene (**2**) under similar conditions.[1]



1 2

It is to be specifically noted that all Ag$^+$-catalyzed reactions examined to the present time have dealt with molecules possessing high levels of structural rigidity. Accordingly, concerted catalyzed reactions in these instances need not necessarily be free (for steric reasons) to proceed along *competitive* symmetry-allowed and -forbidden pathways. Such considerations have caused van der Lugt[6] to conclude that "orbital symmetry seems not relevant for explaining the lowering of the energy of activation of forbidden reactions catalyzed by a transition metal." Resolution of this issue was deemed imperative and we have therefore examined the stereochemical course of the Ag$^+$-catalyzed isomerization of two structurally unconstrained hydrocarbons, the *endo*,*exo*- (**3**) and *exo*,*exo*-2,4-dimethylbicyclo[1.1.0]butanes (**6**).[7] During this study, unequivocal evidence has been gained that bicyclobutanes rearrange to 1,3-dienes preferentially by a formal $[_\sigma2_a + {}_\sigma2_a]$ pathway; that is to say that excited-state behavior (in the orbital symmetry sense) is exhibited even in those cases where the alternative stereochemical products are of comparable energy content. Also, in-depth kinetic studies of the conversion of **1** to **2** have now resolved the question of the intervention of silver–bicyclobutane complexes.

Addition of **3** to anhydrous silver fluoroborate in deuteriochloroform at ~40° (nmr probe conditions) resulted in highly stereospecific conversion to *cis*,*trans*-2,4-hexadiene (**4**, 62%—containing 0–1% **7**) and to dimer formation (**5**, two isomers in a ratio of 1:1, 38%).[8] The related exo,exo derivative **6** led analogously to dienes **4** and **7** (14%, ratio 1:3) and dimers **8** (two different isomers in a ratio of 1.5:1, 86%).[8] Kinetic measurements relating to the rates of disappearance of **1**, **3**, and **6** are listed in Table I. The assigned structures to dimers **5** and **8** (of differing geometric and configurational stereochemistry) follow convincingly from their high-resolution mass spectra, their nmr features, and independent catalytic hydrogenation to 4,7-dimethyldecane.[9] These "dimers" do not arise from any of the combinations diene + diene, diene + cyclobutene, cyclobutene + cyclobutene, and cyclobutene + bicyclobutane; in actuality, **4** and **7** as well as *cis*- (**9**) and *trans*-3,4-dimethylcyclobutenes (**10**)[10] are stable to the reaction conditions. Consequently, **9**



$$\mathrm{CH_3CH{=}CH\overset{\displaystyle CH_3}{\overset{|}{C}}HCH{=}CH\overset{\displaystyle CH_3}{\overset{|}{C}}HCH{=}CHCH_3}$$

7 8

$$\mathrm{CH_3CH{=}CH\overset{\displaystyle CH_3}{\overset{|}{C}}HCH{=}CH\overset{\displaystyle CH_3}{\overset{|}{C}}HCH{=}CHCH_3}$$

Table I. Isomerization Rate Data (C_6H_6 Solution)[a]

Hydrocarbon	$AgClO_4$, N	T, °C	k_{Ag}, M^{-1} sec^{-1}	Rel rate
1	7.86×10^{-2}	30.00	9.8×10^{-4}	
	7.86×10^{-2}	40.00	2.8×10^{-3}	1
	3.43×10^{-2}	50.00	6.8×10^{-3}	
3	4.03×10^{-2}	40.1	6.5×10^{-3}	2.3
6	2.02×10^{-2}	40.1	1.4×10^{-2}	5

[a] These rate data pertain to the initial rate of disappearance of bicyclobutane.

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[1] Paper IV: L. A. Paquette, G. R. Allen, Jr., and R. P. Henzel, *J. Amer. Chem. Soc.*, **92**, 7002 (1970).

[2] L. Cassar, P. E. Eaton, and J. Halpern, *ibid.*, **92**, 6366 (1970).

[3] L. A. Paquette and J. C. Stowell, *ibid.*, **92**, 2584 (1970).

[4] (a) L. A. Paquette, *ibid.*, **92**, 5765 (1970); (b) W. G. Dauben, M. G. Buzzolini, C. H. Schallhorn, D. L. Whalen, and K. J. Palmer, *Tetrahedron Lett.*, 787 (1970); (c) R. Askani, *ibid.*, 3349 (1970).

[5] L. A. Paquette, R. S. Beckley, and T. McCreadie, submitted for publication.

[6] W. Th. A. M. van der Lugt, *Tetrahedron Lett.*, 2281 (1970).

[7] G. L. Closs and P. E. Pfeffer, *J. Amer. Chem. Soc.*, **90**, 2452 (1968).

[8] Percentage compositions were determined by quantitative integration of nmr spectra. Vpc analysis was utilized to establish the ratio of dimers and dienes. The structures assigned to dienes **4** and **7** are based on comparison of spectral data with authentic samples obtained from Chemical Samples Co., Columbus, Ohio. Additionally, nmr spectra are identical with those provided by Dr. R. Srinivasan (IBM), whom we thank.

[9] Authentic 4,7-dimethyldecane was synthesized by catalytic hydrogenation (10% Pd/C, CH_3OH, 50°, 50 psig) of 4,7-dimethyl-5-decyne-4,7-diol (K + K Laboratories) according to the method of R. J. Tedeschi, *J. Org. Chem.*, **27**, 2398 (1962).

[10] R. E. K. Winter, *Tetrahedron Lett.*, 1207 (1965). We thank Professor Winter for a sample of **9** and directions for an improved synthesis of **10**.