NH_4OH, to remove unreacted metal salts. They were then washed with methanol and acetone to remove unreacted ligand. The compounds were dried in a vacuum desiccator over $CaCl_2$, ground, and soxhleted with acetone and/or methanol for 2 or 3 days until clear.

Anal. Calcd for $Cu_2(C_{19}H_{14}O_4)_2 \cdot H_2O$: C, 60.72; H, 3.73; Cu, 16.91. Found: C, 60.85; H, 3.70; Cu, 16.51. Calcd for $Cu_3(C_{19}H_{13}O_4)_2(H_2O)_3$: C, 53.61; H, 3.76; Cu, 22.40. Found: C, 53.44; H, 3.80; Cu, 22.51. Calcd for $Ni_2(C_{19}H_{14}O_4)_2(H_2O)_4 \cdot H_2O$: C, 55.65; H, 4.76; Ni, 14.32. Found: C, 55.44; H, 4.65; Ni, 14.15. Calcd for $Ni_3(C_{19}H_{13}O_4)_2(H_2O)_6$: C, 50.99; H, 4.28; Ni, 19.69. Found: C, 50.35; H, 4.41; Ni, 19.80. Calcd for $Co_3(C_{19}H_{13}O_4)_2(H_2O)_6$: C, 50.95; H, 4.25; Co, 19.70. Found: C, 51.11; H, 4.22; Co, 19.13.

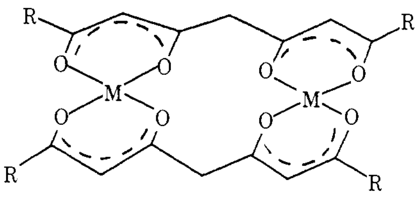
The infrared spectra of these compounds are all very similar. None of the spectra exhibit absorptions due to free, unchelated carbonyl groups. Even the compounds containing only two metal ions do not contain "free carbonyls" as evidenced by their infrared spectra.

Preliminary magnetic susceptibility measurements between 77 and 300°K have uncovered several interesting features (Table I). For example, the moment of $Cu_3(DBAA)_2(H_2O)_3$ is unusually low indicating inter- as well as intramolecular exchange, the high moments for $Ni_3(DBAA)_2(H_2O)_6$ are perhaps due to quite strong ferromagnetic exchange, and the temperature dependence of the $Co_3(DBAA)_2(H_2O)_6$ magnetic moments are indicative of reasonably strong antiferromagnetism. All of these features are under more detailed study.

Table I. Magnetic Moments (BM) Reported on a Per Metal Basis

	300°K	276°K	195°K	77°K
$Co_3(DBAA)_2(H_2O)_6$	4.71		4.66	4.09
$Cu_3(DBAA)_2(H_2O)_3$	0.90	0.82	0.63	0.49
$Cu_2(HDBAA)_2 \cdot H_2O$	1.89	1.80	1.78	1.63
$Ni_3(DBAA)_2(H_2O)_6$	3.95	3.74	3.52	3.35
$Ni_2(HDBAA)_2(H_2O)_4 \cdot H_2O$	3.14		3.08	2.88

While structural data for these complexes have not yet been obtained, certain aspects seem clear from the magnetic data and by analogy to the structure of the 1,3,5-triketonates. First, it is most probable that the $DBAA^{3-}$ ligand is planar due to the presence of sp^2 hybridized carbons. The planarity of coordinated 1,3,5-triketonates has been established by a single-crystal X-ray structure determination of bis(1,5-diphenyl-1,3,5-pentanetrionato)tetra(pyridine)dicobalt(II).[5] Indeed, the two Co atoms and the six oxygens are coplanar within experimental error. It is reasonable that these structural features be carried over to the tetraketonates as well. Second, the complexes with only two metal ions appear to have the metals separated rather than adjacent to one another. This conclusion is supported by the lack of "free carbonyl" absorptions in the infrared spectra and the nearly normal room temperature magnetic moments. Thus, of the three probable structures shown below, **1** or **2** seem most reasonable. (Note: H_2O has been omitted for simplicity.) The somewhat depressed magnetic moments of the binuclear complexes at 77°K may be due to exchange through the bridging ligand systems of **1** and **2**. It is clear, however, that if the metals were in the environment shown in **3** much different magnetic behavior would be expected. Since the magnetic behavior is not at all similar to analogous 1,3,5-triketonates[2-4] we have discounted **3** as a possibility. For structure **1** or **2** the interesting possibility exists that a third metal ion could be placed in the vacant site. From the standpoint of magnetic exchange studies it would be most interesting if the third metal ion were different from the original two.



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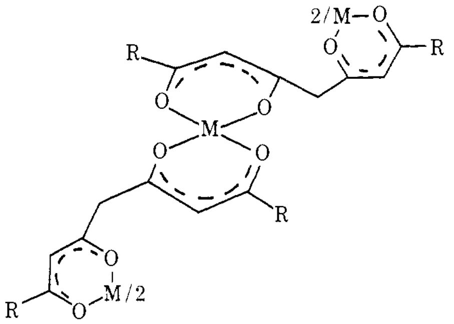

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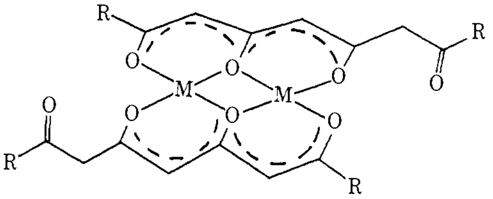

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A Novel Electrocyclic Process. Facile Generation of a Diazacyclopentadienone

Sir:

The decomposition of bisdiazo compounds as a route to strained olefins has met with limited success.[1,2] We have shown that the photochemical decomposition of 1,3-bisdiazo-1,3-diphenyl-2-propanone produces diphenylcyclopropenone as the major initial product

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[1] P. J. Whitman and B. M. Trost, *J. Amer. Chem. Soc.*, **91**, 7534 (1969).

[2] K. Geibel and H. Maeder, *Chem. Ber.*, **103**, 1645 (1970); T. Lieser and G. Geck, *ibid.*, **83**, 137 (1960); J. Font, F. Serratosa, and J. Vallis, *Chem. Commun.*, 721 (1970); M. Regitz and H. J. Geelhaar, *Chem. Ber.*, **102**, 1743 (1969).

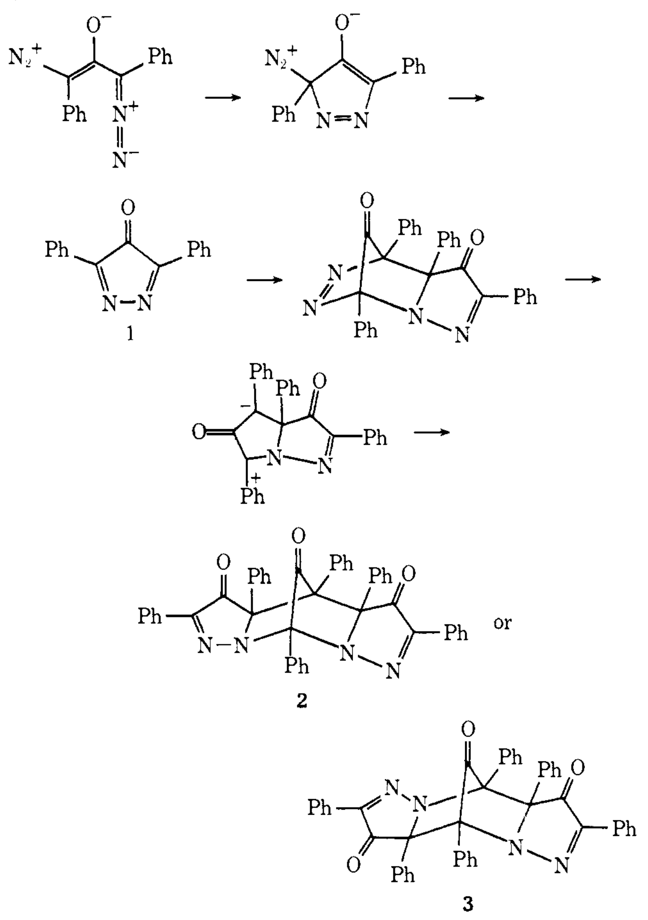
upon irradiation presumably *via* intramolecular trapping of a carbene intermediate. In this communication, we wish to report the contrasting fascinating thermal behavior of this bisdiazo compound which involves a novel electrocyclic ring closure and provides a simple route to 3,4-diaza-2,5-diphenylcyclopentadienone (**1**), a member of a much sought after class of compounds.[3,4]

Allowing a hexane solution of 1,3-bisdiazo-1,3-diphenyl-2-propanone[1] to stand at room temperature effects the evolution of gas accompanied by the disappearance of the red color of the starting material and the formation of an insoluble yellow solid, mp 206–208°. This yellow solid has a molecular formula of $C_{45}H_{30}N_4O_3$ on the basis of its elemental analysis (Found: C, 80.02; H, 4.56; N, 8.26), mass spectrum (M^+ at *m/e* 674), and osmometric molecular weight (mol wt 676).[5] The infrared spectrum shows a strained carbonyl (1805 cm^{-1}) and α-ketoimine (1733 and 1672 cm^{-1}). The proton nmr spectrum shows only aromatic proton absorptions between δ 7.20 and 7.80. The mass spectrum was most informative. It shows a strong peak for the loss of diazadiphenylcyclopentadienone at *m/e* 440.15493 ($C_{30}H_{20}N_2O_2$) with the appropriate metastable (*m/e* 81.5) for 674 $\rightarrow$ 234 + 440. The 440 fragment cleaves into a dihydrodiazadiphenylcyclopentadienone (*m/e* 236 with metastable at *m/e* 126.8) and tolan radical cation (*m/e* 178). These data are in accord with either structure **2** or **3** in Scheme I. A decision in favor of **2** arises from the ^{13}C nmr spectrum which shows three types of sp^3 carbons at 75.6, 80.8, and 87.2 ppm downfield from TMS, whereas compound **3** would show only two types of sp^3 carbons. That the compound has only two kinds of carbonyl carbons at 191.5 and 192.7 demonstrates that it is either a bis endo or bis exo adduct but not an endo–exo isomer.

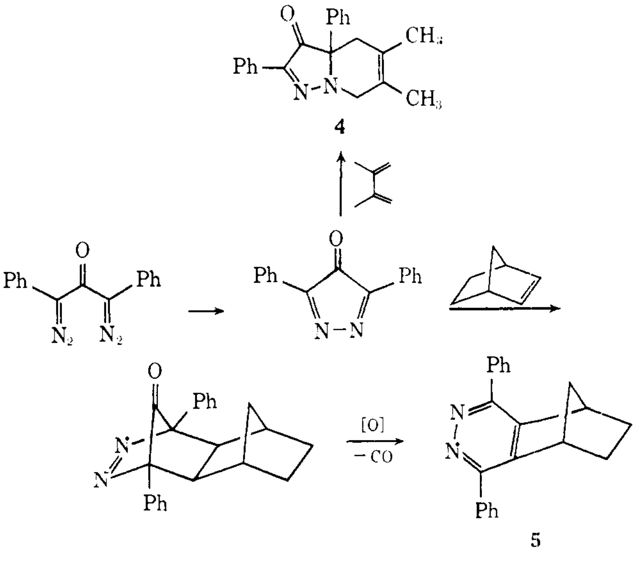
The formation of **2** quantitatively is best rationalized *via* the intermediacy of 3,4-diaza-2,5-diphenylcyclopentadienone as outlined in Scheme I. Since the decomposition of the bisdiazo compound *via* carbene routes leads exclusively to products derived from initial 1,3 bonding,[1] the formation of **1** is best described as an electrocyclic closure isoelectronic with the pentadienyl to cyclopentenyl anion cyclization[6] followed by nitrogen elimination.[7]

The intermediacy of **1** is confirmed by diverting the reaction in the presence of traps. Thus, allowing the bisdiazo compound to decompose in the presence of 2,3-dimethylbutadiene or norbornene generated 3,4-dimethyl-6,8-diphenyl-1,9-diazabicyclo[4.3.0]nona-3,8-dien-9-one (**4**), mp 157–159° (lit.[4] mp 159–160°), and 1,4-diphenyl-5,8-methylene-5,6,7,8-tetrahydrophthalazine (**5**), mp 229–230° (lit.[4] mp 230.5–231.5°) in 85 and 91% yields, respectively (see Scheme II). The facility of preparation of the bisdiazo compound directly from 1,3-diphenyl-2-propanone and the high yields of trapping products in the thermal decomposition clearly make this method the one of choice for utilization of 3,4-diaza-1,3-diphenylcyclopentadienone in synthesis.

Scheme I. Thermal Decomposition of 1,3-Bisdiazo-1,3-diphenyl-2-propanone



Scheme II. Trapping of 3,4-Diaza-2,5-diphenylcyclopentadienone



Acknowledgment. We wish to thank the National Science Foundation for their generous support of our work. We thank Drs. George Levy and Philip Kinson

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(3) For earlier attempts to prepare 3,4-diazacyclopentadienones, see J. P. Freeman and J. J. Gannon, Jr., *J. Heterocycl. Chem.*, 3, 544 (1966); J. P. Freeman and D. L. Surbey, *Tetrahedron Lett.*, 4917 (1967); M. J. Nye and W. P. Tang, *Can. J. Chem.*, **48**, 3563 (1970).

(4) For a successful approach, see P. J. Fagan and M. J. Nye, *Chem. Commun.*, 535 (1971).

(5) Instrument standardized with tris(3,5-di-*tert*-butyl-4-oxo-2,5-cyclohexadien-1-ylidene)cyclopropane.

(6) R. B. Bates and D. A. McCombs, *Tetrahedron Lett.*, 977 (1969).

(7) The closest analogy for such a process is the conversion of 1,3-diazopropane and vinyldiazomethane to pyrazoline: H. Hart and J. L. Brewbaker, *J. Amer. Chem. Soc.*, **91**, 707 (1969).

of the General Electric Company for the obtention of the ^{13}C nmr spectrum.

(8) Camille and Henry Dreyfus Teacher–Scholar Grant Recipient.
(9) National Institutes of Health Predoctoral Fellow.

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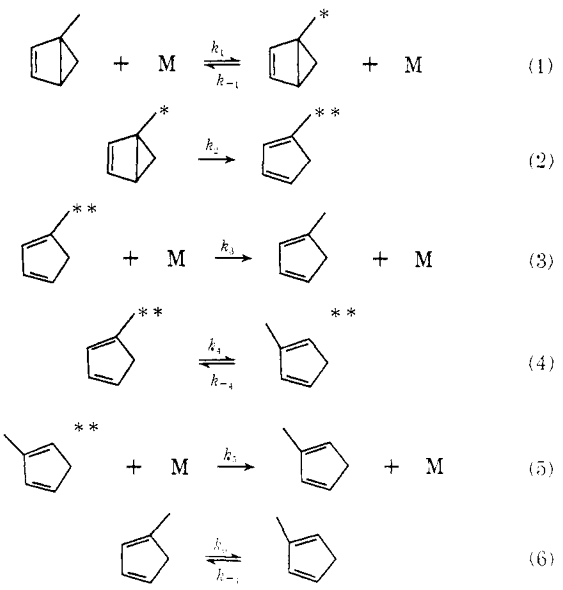
Hot Molecule Effects in the Thermal Isomerization of Methylbicyclo[2.1.0]pent-2-enes

Sir:

There is a controversy about the mechanism of the isomerization of bicyclo[2.1.0]pent-2-ene to cyclopentadiene. Originally a biradical process was proposed.[1,2] Later experiments[3] with deuterated bicyclopentene and 2-methylbicyclo[2.1.0]pent-2-ene were interpreted as conclusive evidence for the occurrence of an allowed [$_\sigma 2_s + {}_\sigma 2_a$] process. The methyl compound results have not been substantiated and diametrically opposite experimental results have been reported.[4] These two sets of data were obtained in the liquid phase. About this work we merely note in passing that even if the allowed process were of major importance the experimental findings of Baldwin and Andrist[3] of only *one* product are inexplicable on kinetic grounds.

The report of some gas-phase results prompts us to present some RRKM calculations that are pertinent. Briefly, Baldwin and Andrews[5] found that in the gas phase at 50°, 1-methylbicyclo[2.1.0]pent-2-ene isomerizes to both 1-methyl- and 2-methylcyclopentadiene. Similarly, 2-methylbicyclo[2.1.0]pent-2-ene gave both methylcyclopentadienes. Since the interconversion between the cyclopentadienes is appreciably slower at 50° than is the isomerization of the bicyclo[2.1.0]pent-2-enes they conclude that the decomposition of each reactant yields both cyclopentadienes directly. This would be consistent with allowed processes (but would not, incidentally, be subject to the kinetic objections mentioned above). These experimental findings are completely explicable on the basis of the initial formation of only *one* isomer (the one predicted by the biradical mechanism) and are exactly as expected. The scheme is shown below for 1-methylbicyclo[2.1.0]pent-2-ene (eq 1–6). Step 1 represents the collisional activation–deactivation process of a unimolecular reaction and steps 3 and 5 simple collisional deactivation steps. Step 6 is a shorthand form and is applicable to all unimolecular reactions in their high-pressure region. Steps 2 and 4 may be treated by RRKM theory.



Reliable Arrhenius parameters are not available for k_6 and k_{-6}; however, calculations have been carried out using the rate constants reported by Baldwin and Andrews[5] at 50° and assuming an "A" factor for both reactions of 10^{13}. Other calculations used an "A" factor of 10^{12}, deliberately chosen to be unrealistically low, and also a further set used different A factors for k_6 and k_{-6} to increase the possible difference in energy of activation of these reactions. The results are presented in Table I. The values of the ratios of 1- and 2-methylcyclopentadienes (A/B) at various pressures correspond to hypothetical "zero time" reactions. In Table II we report the time evolution of the system.

Table I. Ratio of 1- to 2-Methylcyclopentadiene as a Function of Pressure

	Pressure, Torr				
	1	10	100	1000	10^6
A/B^a	0.937	0.939	0.951	1.07	140
A/B^b	0.938	0.944	1.01	1.639	670
A/B^c	1.647	1.650	1.670	1.870	220

[a] Assuming $\log k_6 = 13 - 26{,}745/\theta$; $\log k_{-6} = 13 - 26{,}967/\theta$. [b] Assuming $\log k_6 = 12 - 25{,}271/\theta$; $\log k_{-6} = 12 - 25{,}493/\theta$. [c] Assuming $\log k_6 = 12.7 - 26{,}299/\theta$; $\log k_{-6} = 13.0 - 26{,}967/\theta$. $\theta = 2.303RT$; $R = 1.987$ cal mol^{-1} K^{-1}.

Table II. Time Evolution of System at 50°

	Time, sec				
	0	500	1000	4000	8000
A/B^a	1.009	1.008	1.006	0.998	0.984
A/B^b	1.639	1.634	1.629	1.593	1.538

[a] At 100 Torr. [b] At 1000 Torr. Data relate to footnote *b* of Table I.

Table I shows that irrespective of the particular choice of Arrhenius parameters the ratio A/B is essentially constant below 100 Torr and does not increase greatly up to 1000 Torr. At very high pressures the ratio of A/B is sufficiently large that little or no 2-methylcyclopentadiene should be formed in the liquid phase in accord with the findings of McLean, *et al.*[4]

The predicted ratio of A/B for runs carried out at around 1 atm pressure is between 1.0 and 1.75 depending on the particular choice of Arrhenius parameters; Baldwin and Andrews[5] obtained 1.6. Within the un-

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(1) J. I. Brauman and D. M. Golden, *J. Amer. Chem. Soc.*, **90**, 1920 (1968).
(2) D. M. Golden and J. I. Brauman, *Trans. Faraday Soc.*, **65**, 464 (1969).
(3) J. E. Baldwin, R. K. Pinschmidt, Jr., and A. H. Andrist, *J. Amer. Chem. Soc.*, **92**, 5249 (1970); J. E. Baldwin and A. H. Andrist, *Chem. Commun.*, 1561 (1970).
(4) S. McLean, D. M. Findlay, and G. I. Dmitrienko, *J. Amer. Chem. Soc.*, **94**, 1380 (1972).
(5) J. E. Baldwin and G. D. Andrews, *ibid.*, **94**, 1775 (1972).