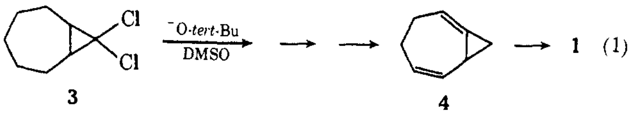
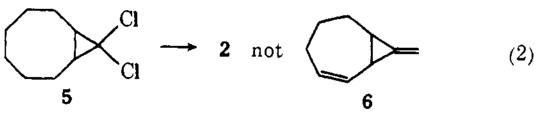
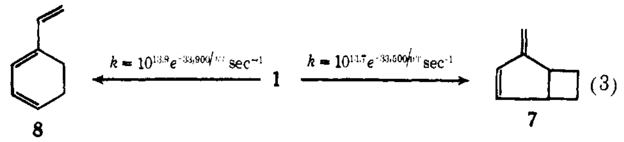
chlorobicyclo[5.1.0]octane (**3**)[4] to a cold solution of potassium *tert*-butoxide in dimethyl sulfoxide. The flash-distilled reaction product was over 90% pure, and further purification was accomplished by preparative scale gas chromatography. The skeletal rearrangement might arise from the intermediacy of the highly strained compound **4**, formed by the normal[5] elimination route, which then suffers a methylenecyclopropane rearrangement, as shown in eq 1.[6]



Compound **2** was similarly prepared by the elimination from 9,9-dichlorobicyclo[6.1.0]nonane[4] (**5**). The rearranged product analogous to **1**, compound **6**, was not obtained, as shown by the reduction to bicyclo-[6.1.0]nonane. Presumably **2** is, by virtue of the larger ring size, far less strained than **4**, accounting for the preparation of **2** and not of **6** by this method, eq 2.

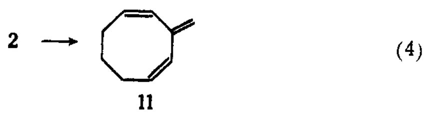


The study of the thermolysis is summarized by eq 3.



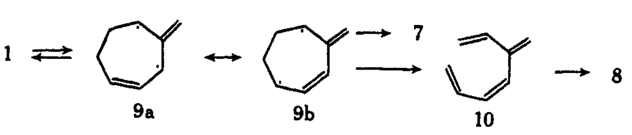
The rates were followed in the gas phase using the diffusively stirred flow system.[7] Both reactions followed a first-order course with the indicated rate constants; the ratio of **7** to **8** was 1.15 ± 0.05 at all temperatures.[8]

Compound **2** rearranges in dimethylformamide to **11**, 3-methylene-1,4-cyclooctadiene, by a first-order process, followed by nmr, giving $k = 10^{11}e^{-29,000/RT}$ sec^{-1}, eq 4.

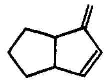


Scheme I conveniently accounts for both **7** and **8** from **1**. The formation of **7** suggests this biradical path, since a one-step thermally allowed 1,3-sigmatropic shift requires an inversion at the migrating center,[9] leading to an unknown trans-fused ring system, and the 3,3-sigmatropic shift, adequate for the parent compound,[5] is impossible. The formation of **7** from **8** is accounted for through the fission[10] of the "1,4" diradical **9b** to the tetraene **10** followed by facile cyclization to **8**. Activation energies sometimes eliminate a diradical mechanism, but the activation energy should be roughly that of *trans*-2-thujene isomerization (44 kcal)[11] less the allyl resonance energy (13 kcal), or 31 kcal,[12] not helpfully different from the observed 33.5 kcal. The same diradical, **9**, is required for the assumed reaction **4** → **1**, and the good yield of **1** requires that **9** have a lower barrier leading to **1** than to **7** or **8**.

Scheme I



The reaction **2** → **11** must involve a hydrogen migration. It may occur by the sequence **2** → **6** → **11**, or by a hydrogen migration in the diradical. An argument against the intermediary of **6** is that its expected rearrangement product, **12**, is undetected.



12

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and the last two signals for the olefinic hydrogens are virtually identical with those of 3-methylene-4-methylcyclopentene. **8** is a known compound (W. Ziegenbein, *Angew. Chem., Int. Ed., Engl.*, **4**, 70 (1965)). Its uv maxima absorption is indistinguishable from that kindly supplied by Dr. Ziegenbein, and the nmr spectrum is consistent. The conjugation of **11** is shown by the λ_{max} 250 nm and the skeleton by hydrogenation to methylcyclooctane, and the nmr is too simple to allow a structure of lesser symmetry [δ 1.44 (m, 2 H), 2.25 (m, 4 H), 4.93 (s, 2 H), 5.33 (double t, 2 H), 6.24 (d, 2 H)].

(4) The dichlorocyclopropanes were prepared following P. S. Skell and A. Y. Garner, *J. Amer. Chem. Soc.*, **78**, 3409 (1956).

(5) T. C. Shields, W. E. Billups, and A. R. Lepley, *ibid.*, **90**, 4749 (1968).

(6) An alternative rearrangement is to homotropylidene, but this product was not found.

(7) E. S. Lewis and J. T. Hill, *J. Amer. Chem. Soc.*, **91**, 7458 (1969).

(8) Another compound, not identified, was produced in <3% yield.

(9) J. A. Berson, *Accounts Chem. Res.*, **1**, 152 (1968).

(10) P. D. Bartlett and N. A. Porter, *J. Amer. Chem. Soc.*, **90**, 5317 (1968).

(11) R. H. Eastman, Final Technical Report, AFOSR Contract No. AF-49-638-1272.

(12) J. S. Swenton and A. Wexler, *J. Amer. Chem. Soc.*, **93**, 3066 (1971).

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Unusual Water Exchange Behavior in Copper(II)- and Nickel(II)-β,β',β''-Triaminotriethylamine Complexes

Sir:

In the course of studying, by means of ^{17}O nmr, the kinetics of a number of water exchange processes in substituted aquo metal ions, we have found unique behavior for Cu(II)- and Ni(II)-tren (β,β',β''-triaminotriethylamine) complexes.

Among the considerable number of Ni(II) complexes studied, we have observed in any given case only one apparent exchange rate for bound water in the partly substituted species. For the Ni(II)-tren species, however, two distinct rates are observed.[1] While the

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(1) A similar result has apparently been found for the Ni(II)-NTA system: private communication from Drs. J. Vriesenga and R. E. Connick.

structure of tren complexes in solution seems to be rather uncertain, our observations suggest that the usual assumption of a cis-octahedral arrangement ($Ni(tren)(H_2O)_2^{2+}$) is correct. The two water molecules in such a structure are in different environments. The results derived from ^{17}O nmr line broadening and paramagnetic shifts are shown in Table I. The slower exchange is about what one would predict from our study of aliphatic amine ligands.[2,3]

Table I. Water Exchange Kinetics in tren Complexes

System	k_1, 25° sec^{-1}	ΔH^*, kcal/mol
$Ni(tren)(H_2O)_2^{2+}$	8.2×10^5	8 ± 1
	$\sim 9 \times 10^{6\,a}$	8 ± 1.5
	1.5×10^6 (−10°)	
$Cu(tren)(H_2O)^{2+}$	2.5×10^5	10.4 ± 0.3

[a] The value at 25° is extrapolated from the more accurate one at −10°.

Substitution of water in the Ni–tren complex by ammonia[4] is fairly consistent with replacement of the faster exchanging water *via* an Eigen mechanism. The reported substitutions on the Ni–tren complex by phen and bipy[5] are slower than for NH_3 by a factor of at least 20. It has been suggested[5] that the rate-determining step with the chelate ligands involves ring closure. Since phen and bipy when attached at one end would not be expected to affect the lability of the remaining water molecule,[5–7] which exchanges relatively slowly, the loss of this water may be rate determining for ring closure. The ratio of water exchange rates at 25° is *ca.* 10–20, which is at least suggestive that the loss of the second water is important here. If this idea is correct, one predicts that ethylenediamine substitution on Ni–tren should be considerably more rapid than for phen or bipy; apparently this reaction has not been studied.

The case of Cu(II) is interesting because of the single relatively slow rate of exchange observed (see Table I), more like Ni(II) than Cu(II). The structure of the complex in aqueous solution is uncertain. Suggestions of trigonal-bipyramidal,[8] tetrahedral,[9] and cis-octahedral[10] structures have been made. Polymeric forms of the Ni(II) complex are reported[11] but the Cu(II) species is said to be monomeric.[8] We have measured the effect of NH_3 addition on the $^{17}OH_2$ line broadening due to the Cu–tren complex. At a 1:1 NH_3/Cu ratio the line broadening becomes very small, suggesting that a monoammine–tren complex (five-coordinate) has formed. This result suggests five coordination also for the aquo–tren complex but, of course, is not conclusive evidence. No shift in the $^{17}OH_2$ resonance was observed for the aquo–tren species which tends to rule out the presence of a second very rapidly exchanging water molecule.

As far as we are aware, no substitution work has been done on the copper complex which can be compared with water exchange.

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(3) J. P. Hunt, *Coord. Chem. Rev.*, 7, 1 (1971).

(4) J. P. Jones, E. J. Billo, and D. W. Margerum, *J. Amer. Chem. Soc.*, **92**, 1875 (1970).

(5) R. G. Wilkins, *Accounts Chem. Res.*, 3, 408 (1970).

(6) M. Grant, H. W. Dodgen, and J. P. Hunt, *J. Amer. Chem. Soc.*, **92**, 2321 (1970).

(7) M. Grant, H. W. Dodgen, and J. P. Hunt, *Inorg. Chem.*, **10**, 71 (1971).

(8) H. B. Jonassen and H. Thilemann, *Z. Anorg. Chem.*, **320**, 274 (1963).

(9) C. R. Bertsch, W. C. Fernelius, and B. P. Block, *J. Phys. Chem.*, **62**, 444 (1958).

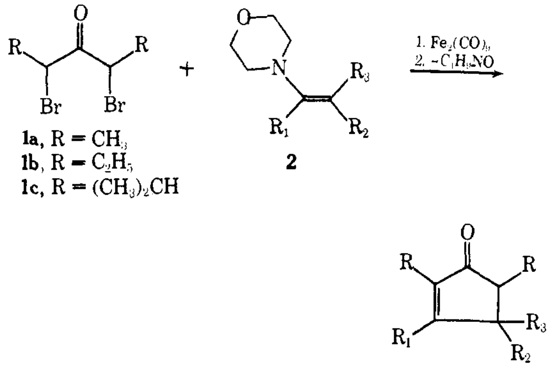
(10) C. K. Jørgensen, *Acta Chem. Scand.*, 10, 887 (1956).

(11) H. B. Jonassen and V. V. Ramanujam, *J. Phys. Chem.*, **63**, 411 (1959).

Reaction of α,α′-Dibromo Ketones and Enamines with the Aid of Iron Carbonyls. A Novel Cyclopentenone Synthesis[1]

Sir:

The construction of five-membered carbocyclic systems has been generally accomplished by intramolecular condensation of open-chain dicarbonyl compounds or dicarboxylic acid derivatives,[2] or ring contraction of six-membered cyclic ketones.[3,4] This paper describes a new, facile cyclopentenone synthesis by *intermolecular* coupling of three- and two-carbon units. The general sequence (eq 1) which consists of reaction of the dibromo ketones **1** and the morpholine enamines **2** in the presence of iron carbonyls, followed by spontaneous elimination of morpholine, was achieved under mild reaction conditions, and usually in satisfactory yield.



1a, $R = CH_3$
1b, $R = C_2H_5$
1c, $R = (CH_3)_2CH$

2

3

(1)

For example, when a mixture of **1a** (10 mmol), α-morpholinostyrene (25 mmol), and $Fe_2(CO)_9$ (12 mmol) in dry benzene (25 ml) was stirred at 25–30° for 12 hr under nitrogen atmosphere, the desired cyclopentenone **3** ($R = CH_3$, $R_1 = C_6H_5$, and $R_2 = R_3 = H$) was obtained in 94% yield after silica gel chromatography: ir (CCl_4) 1696 (C=O) and 1626 cm^{-1} (C=C); uv (C_2H_5OH) 220 (log ε 3.72) and 279 nm (4.05); nmr (CCl_4)

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(2) (a) A. T. Nielsen and W. J. Houlihan, *Org. React.*, **16**, 1 (1968); (b) R. A. Raphael, "Chemistry of Carbon Compounds," Vol. IIA, E. H. Rodd, Ed., Elsevier, New York, N. Y., 1953, p 71; (c) M. Green, G. R. Knox, and P. L. Pauson, "Rodd's Chemistry of Carbon Compounds," Vol. IIA, S. Coffey, Ed., Elsevier, New York, N. Y., 1967, p 104.

(3) For example, B. G. McFarland, "Steroid Reactions," C. Djerassi, Ed., Holden-Day, San Francisco, Calif., 1963, p 427.

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